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Survey of Degradation Modes of Candidate Materials for High-Level Radioactive-Waste Disposal Containers

Volume 5
Localized Corrosion of Copper-Based Alloys

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Acronyms

BNFMRA	British Nonferrous Metals Research Association
CDA	Copper Development Association
CEBELCOR	Centre Belge d'Etude de la Corrosion
ESCA	electron spectroscopy for chemical analysis
IGSCC	intergranular stress corrosion cracking
INCRA	International Copper Research Association
LC	localized corrosion
NHE	normal hydrogen electrode
NNWSI	Nevada Nuclear Waste Storage Investigations Project
SCC	stress corrosion cracking
SCE	saturated calomel electrode
TGSCC	transgranular stress corrosion cracking

Executive Summary

This volume reports on the available data regarding localized corrosion (LC) of three copper-based alloys: CDA 102, CDA 613, and CDA 715. These three alloys are candidates for fabrication of high-level radioactive-waste disposal containers to be used at the prospective repository at Yucca Mountain, Nevada. The corrosion properties of austenitic alloys that are being considered are reviewed in Vol. 3. LC phenomena include pitting, crevice corrosion, intergranular stress corrosion cracking, and transgranular stress corrosion cracking.

Section 1 of this volume provides a brief introduction to the anticipated environmental conditions at the repository and the degradation modes expected, which include atmospheric oxidation, uniform aqueous phase corrosion, and various forms of LC. The selection of the candidate material that is expected to give adequate performance under anticipated repository conditions will be based on three criteria: a literature survey, corrosion testing, and predictions from modeling. This volume is a critical survey of the literature on LC of the copper-based candidates.

Section 2 discusses the metallurgical properties of copper-based alloys and their applications. These alloys have been used in roofing, plumbing tube and fittings, heat exchangers, and semiconductor packages. Copper-based alloys have also been incorporated in equipment used in desalination plants, power plants, and industrial and chemical plants.

Section 3 reviews the environment expected in the repository, with an emphasis on specific ions that might affect pitting of these alloys, namely, S^{2-}, HS^-, HCO_3^-, SO_4^{2-} Cl^-, Fe^{3+}, and H^+. The type of pitting observed on copper depends on the bicarbonate-to-sulfate ratio. Section 4.1 reviews the types of pitting seen in fresh water and seawater. The data from seawater experiments may be relevant to situations involving the concentration of ionic species in groundwater by refluxing on hot container walls. Two types of pitting are seen in fresh water. Type 1 pitting is usually associated with hard or moderately hard well waters, and is more likely to affect cold-water pipes. Type 2 pitting occurs in some soft-water areas and is basically nonexistent if the water temperature is below 60°C (140°F). While both types of pitting are seen in fresh water, Type 2 pitting has not been reported in seawater.

The effect of surface condition (as manufactured) on pitting is discussed in Sec. 4.2. Surface condition appears to have no influence on Type 2 pitting but is of major importance in Type 1 pitting. The surface conditions studied include carbon films and cuprous oxide films formed during annealing. The effect of composition on pitting is reviewed in Sec. 4.3. Copper with just 1% tin or aluminum is more resistant to pitting in the presence of carbon residues than is ordinary commercial copper. Section 4.4 discusses the effect of temper, which is associated with effects of surface conditions arising from differences in manufacturing procedures.

Section 4.5 provides an overview of the mechanisms involved in pitting, of which there are two views. One is that oxygen reduction occurs on a large cathodic area on the surface of copper, and pitting occurs on a small anodic area. The other view presumes that oxygen reduction occurs above the pit, not on the surrounding area. Local accumulation of corrosion products, resulting from general attack on the copper surface, is thought to produce pitting. The thermodynamic stability of passive films on copper is discussed, and potential-pH diagrams are provided for various systems (for example, $Cu\text{-}Cl\text{-}H_2O$ and $Cu\text{-}CO_2\text{-}H_2O$). Some experimental studies of oxide films are reviewed for copper in other environments, namely in solutions of $Cu(ClO_4)_2$ and $Cu(CHO_2)_2$. These studies found differences in growth rates on different crystal faces, which are believed to be due to corresponding differences in film morphology. The section concludes with a review of several studies on the critical pitting potential for localized breakdown of passive films.

Section 5.1 reviews the pitting of aluminum bronze, a specialized form of pitting (if it occurs locally) in which binary aluminum bronzes containing more than about 9% aluminum are likely to undergo selective attack similar to dezincification, known as dealuminification. The pitting of the 70/30 cupronickel alloy and the 90/10 cupronickel alloy is discussed in Sec. 5.2. The 90/10 cupronickel alloy is generally considered to be more resistant to pitting corrosion since it forms a somewhat less protective film, which, if pitting develops, results in broader and shallower pits.

The thermodynamic stability of passive films on copper-based alloys is discussed in Sec. 5.3. Pourbaix diagrams for aluminum and nickel are used as a basis of the discussion because such diagrams have not been found for copper-aluminum and copper-nickel alloys. Experimental studies of films on aluminum bronze and cupronickel alloys are reviewed in Sec. 5.4. These studies were performed using various electrochemical techniques, including the scratch test and linear polarization. An equation for growth rate of films, expressed as the anodic current transient, is given in this section. Section 5.5 reviews the localized dealloying of alloy surfaces, which can result in pitting, and shows that the copper-nickel alloys are less susceptible to dealloying than are the copper-aluminum alloys. The kinetics of dealloying are primarily controlled by electrochemical factors, not by solid state diffusion.

Section 6 discusses crevice corrosion, which is a form of localized attack that occurs in occluded areas on metal surfaces exposed to certain environments. Much of the interpretation of crevice corrosion is associated with a concentration cell. This concept is based on the fact that initiation and propagation of localized attack on metal surfaces are influenced by nonuniformity of the corrosive solution. For example, variations in the concentrations of ions or dissolved gases might arise because of crevices that are inaccessible to fresh electrolyte. A difference in potential can result that can influence electrode kinetics to the extent that an electrochemical cell is established, wherein an oxidation process (corrosion) occurs at anodic sites at accelerated rates. The types of cells discussed are the metal-ion concentration cell, the differential aeration cell, the active-passive cell, and other concentration cells (hydrogen-ion, neutral-salt, and inhibitor cells). The mechanism of crevice corrosion is also discussed. The remainder of Sec. 6 discusses the effect of crevice corrosion on other forms of localized attack and the prevention of crevice corrosion (by proper engineering design). The candidate materials are tentatively ranked on the basis of their susceptibility to crevice corrosion.

Section 7 reviews the conclusions of an article on the application of copper-based alloys in marine structures and equipment; the article includes a ranking of the three alloys. Section 8 gives the conclusions of this report, which are based on all of the data discussed, and the following tentative ranking of the alloys:

Pitting corrosion:	CDA 102 = CDA 715 (best) > CDA 613 (worst)
Local dealloying:	CDA 102 (best) > CDA 715 > CDA 613 (worst)
Crevice corrosion:	CDA 715 = CDA 613 (best) > CDA 102 (worst)
Biofouling:	CDA 102 (best) > CDA 715 = CDA 613 (worst)

No data were found on the effects of gamma irradiation on the LC of copper or copper-based alloys.

Note that much of the data in this report is for solutions having higher ionic strengths than those expected in the groundwater near the repository. These data are believed to be relevant, however, since refluxing can concentrate water falling onto container surfaces.

Survey of Degradation Modes of Candidate Materials for High-Level Radioactive-Waste Disposal Containers

Volume 5: Localized Corrosion of Copper-Based Alloys

Abstract

Three copper-based alloys, CDA 102 (oxygen-free, high-purity copper), CDA 613 (aluminum bronze), and CDA 715 (Cu-30Ni), are candidates for the fabrication of high-level radioactive-waste disposal containers. Waste will include spent fuel assemblies from reactors as well as borosilicate glass, and will be sent to the prospective repository site at Yucca Mountain in Nye County, Nevada.

The decay of radionuclides will result in the generation of substantial heat and in fluxes of gamma radiation outside the containers. In this environment, container materials might degrade by atmospheric oxidation, general aqueous phase corrosion, localized corrosion (LC), and stress corrosion cracking (SCC). This volume is a critical survey of available data on pitting and crevice corrosion of the copper-based candidates. Pitting and crevice corrosion are two of the most common forms of LC of these materials. Data on the SCC of these alloys is surveyed in Vol. 4.

Pitting usually occurs in water that contains low concentrations of bicarbonate and chloride anions, such as water from Well J-13 at the Nevada Test Site. Consequently, this mode of degradation might occur in the repository environment. Though few quantitative data on LC were found, a tentative ranking based on pitting corrosion, local dealloying, crevice corrosion, and biofouling is presented.

CDA 102 performs well in the categories of pitting corrosion, local dealloying, and biofouling, but susceptibility to crevice corrosion diminishes its attractiveness as a candidate. The cupronickel alloy, CDA 715, probably has the best overall resistance to such localized forms of attack.

1. Introduction

As discussed in previous volumes, austenitic alloys and copper-based materials are being considered as candidates for fabrication of the metal containers (barriers) for disposal of high-level radioactive waste at the Yucca Mountain site in Nevada. Austenitic materials include Types 304L and 316L stainless steels and Alloy 825 (which is a predominately nickel alloy). Copper-based alloys include CDA 102 (oxygen-free copper), CDA 613 (Cu-7Al), and CDA 715 (Cu-30Ni). These candidate materials must maintain substantially complete containment for at least 300 yr and perhaps as long as 1000 yr. During the first 50 yr after emplacement, the waste-package container must be retrievable from the disposal site [1, 2]. Retrieval entails removing the container with waste from the repository, possibly for reprocessing spent fuel.

Radioactive decay of the stored waste will result in substantial heat generation. Initially, many of the waste packages will be at a temperature of about 250°C. After 100 yr of storage, the temperature will drop to about 150°C. Candidate materials may undergo any of several modes of degradation in the repository environment, including atmospheric oxidation, uniform aqueous phase corrosion, and various forms of localized corrosion (LC). LC phenomena include pitting, crevice corrosion, intergranular stress corrosion cracking (IGSCC), and transgranular stress corrosion cracking (TGSCC). Corrosion phenomena can also be influenced by the radiation field that exists in close proximity to the barrier. Radiolysis of salt-containing condensate films and air generates ionic, free radical, and molecular species that are not present under nonirradiated conditions.

The Metal Barrier Selection and Testing Task of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project has as its objective the selection of a candidate material that will meet the requirements set forth in the relevant federal regulations [1, 2]. This selection will be based on a survey of the literature, corrosion testing at Lawrence Livermore National Laboratory and other locations, and predictions from models. Relevant literature on LC of the three copper-based alloys is reviewed in this volume, and the candidates are ranked in order of their susceptibility to this mode of degradation. A discussion on the methodology and extent of the literature search and on the selection of references can be found in the Overview.[*] Much of the literature reviewed in this volume is printed nearly verbatim from the identified sources.

2. Applications of Copper-Based Alloys

As discussed in Vol. 4, copper and copper-based alloys possess many desirable metallurgical properties. Among them are the following: a wide range of attainable mechanical properties, superior thermal conductivity, ease of fabricating and joining, excellent corrosion resistance, and resistance to biofouling [3, 4]. Background data on the composition and mechanical properties of the materials under consideration here are summarized in Table 1 [5, 6].

An abundance of historical data exists on the long-term durability of copper. For example, artifacts made of copper and copper-based alloys have been found in nearly pristine condition after having been buried in the earth for thousands of years [7]. Furthermore, copper roofing in rural atmospheres has been found to corrode at rates of less than 0.4 mm in 200 yr [7]. Copper-based alloys have also been used in numerous modern-day applications. There are architectural uses for which resistance to atmospheric corrosion is required, such as roofing, building fronts, grillwork, handrails, lock bodies, doorknobs, and kick plates. Copper materials are frequently used in freshwater supply lines and plumbing fittings, for which superior resistance to corrosion by various types of water and soil is important [8]. Cohen and Lyman have recently stated that over 300,000 miles of copper plumbing tube goes into use each year in the

Table 1. Properties of copper-based candidate alloys.

Alloy	Cu (%)	Al (%)	Ni (%)	Fe (%)	Pb (%)	Sn (%)	Mn (%)	Zn (%)	TS[a] (10^3 lb/in.^{2})	YS[a] (10^3 lb/in.^{2})	E[a] (%)
CDA 102	99.95 (min)	—	—	—	—	—	—	—	34	10	45
CDA 613	92.7 (nom)	6.0–8.0	0.5	3.5 (max)	—	0.2–0.5	0.5 (max)	—	80	40	40
CDA 715	69.5 (nom)	—	29.0–33.0	0.4–0.7	0.5 (max)	—	1.0 (max)	1.0 (max)	55	20	45

[a] TS, YS, and E are the tensile strength, yield stress, and the elongation, respectively, for annealed materials.

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[*] J. C. Farmer, R. D. McCright, J. N. Kass, *Survey of Degradation Modes of Candidate Materials for High-Level Radioactive-Waste Disposal Containers, Overview*, Lawrence Livermore National Laboratory, Livermore, California, UCID-21362 Overview (1988).

United States alone. With production on that scale, a failure rate of one tube in every 10,000 or even 100,000 is a very strong inducement to include these materials as candidates [9, 10].

The outstanding corrosion and biofouling resistance of these materials in seawater has resulted in their widespread use in marine service for applications such as pipes, heat exchangers, shafting, and valve stems [11–20]. Applications of these materials have also arisen in desalination plants [21–26], heat exchangers in power plants [27–32], and equipment in industrial and chemical plants [33–38]. Copper is used almost exclusively in electrical wiring and printed circuit boards. (Note: aluminum wiring is sometimes used in buildings.) Other copper-based alloys are used in semiconductor packages, lead frames, and connectors.

3. Environment

Figure 1 summarizes important features of the repository environment [5]. Note that the water is expected to have a near-neutral pH, about 10 ppm chloride, about 20 ppm sulfate, about 120 ppm bicarbonate, dissolved oxygen, and some nitrate. The gamma dose rate around the high-level radioactive-waste containers will be 10^2 to 10^4 rad/hr for the first 50 yr, depending on the waste type, age of the waste, and several design features of the waste package. Gamma radiolysis of air and water in close proximity to the containers can result in the formation of hydrogen peroxide and nitrate, nitrite, and hydrogen ions in solution. Hydrogen ions produced by radiolysis would only be a problem in occluded areas.

4. Pitting of Copper

The copper-based candidate materials are sensitive to several species that might exist in the repository environment. Ions known to play an important role in pitting include S^{2-}, HS^-, HCO_3^-, SO_4^{2-}, Cl^-, Fe^{3+}, and H^+ [9]. Dissolved O_2 is also very important. Pitting of copper and copper-based alloys can occur in both chloride and bicarbonate solutions. In addition to the reduction of oxygen, the reduction of ferric ion to ferrous ion can serve to depolarize anodic reactions involved in pitting and stress corrosion cracking (SCC). Consequently, it is also important to measure concentrations of ferric and ferrous ions in solutions used in testing copper-based alloys. The type of pitting observed depends on the $[HCO_3^-]:[SO_4^{2-}]$ ratio, so measurements of sulfate concentration are important.

Copper tubes are used widely for potable and supply water. Campbell first described pitting of copper tubes in contact with water in 1950 [39]. Extensive investigations have since been conducted with various natural waters because of the practical importance of this problem. Not only is copper susceptible to pitting, but copper alloys such as brasses [40, 41], bronzes [42], and some cupronickels—for example, the 70/30 cupronickel (Cu-30Ni) [43]—are subject to attack. Pitting of copper occurs not only in chloride-containing solutions, but in bicarbonate solutions as well [44].

4.1 Types of Pitting

According to Campbell, there are two types of pitting of copper in fresh water [9, 45, 46]. Numerous papers have been published on this topic, so it is helpful to categorize published work according to the type of pitting discussed. Such classification allows one to easily understand and correlate results. Campbell states [9]:

> Type 1 pitting is usually associated with certain hard or moderately hard well waters. It is more likely to affect cold water pipes than hot water pipes and may cause perforation in only one or two years. It is characterized by the formation of fairly large, well-defined pits usually containing soft crystalline cuprous oxide, and often cuprous chloride, beneath hard green mounds of calcium carbonate and basic copper carbonate. The surface between the

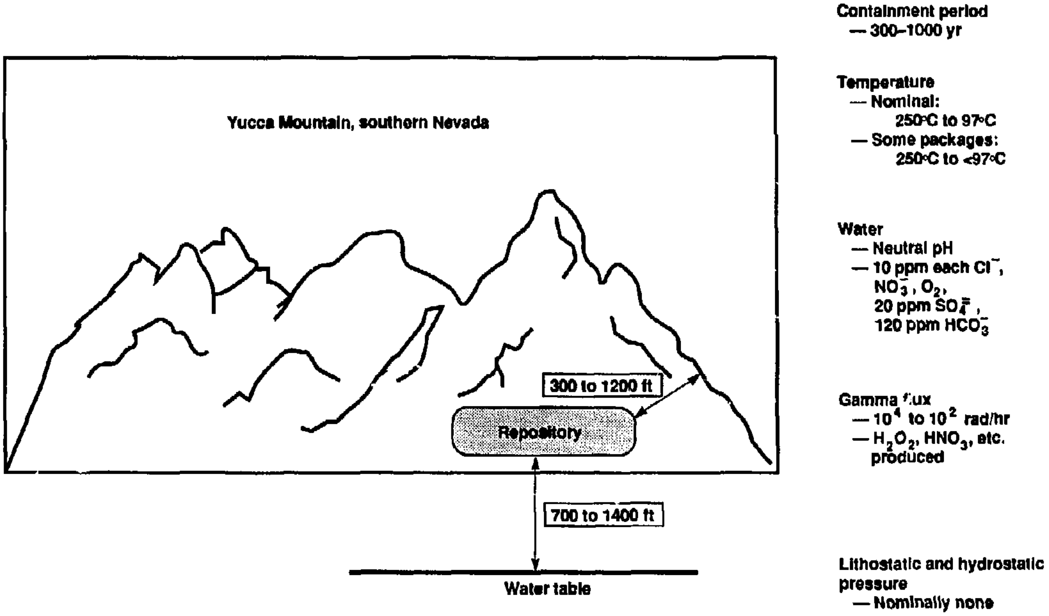

Figure 1. Waste package environment [5].

> pits is often covered with a shiny, dark red, water formed cuprous oxide layer beneath a greenish deposit of hardness salts stained with traces of copper corrosion product. Type 2 pitting occurs only in certain soft water areas and is practically unknown if the water temperature is below 60°C (140°F). It is characterized by deep pits of small cross section, containing very hard crystalline cuprous oxide and capped by small black or greenish-black mounds of cuprous oxide and basic copper sulfate. The surface between the pits usually carries a nearly black layer of water formed oxide (a mixture of cupric and cuprous oxides) beneath a thin layer of silt deposited by the water. Some hot soft waters containing small amounts of manganese can produce a special form of Type 2 pitting in which the pits are larger than those formed during ordinary Type 2 pitting and the black deposit on the surrounding areas of the copper is largely manganese dioxide.
>
> Generally, papers emanating from the United States, Belgium, or Holland, and most of those from the United Kingdom are concerned with Type 1 pitting; papers from Sweden are concerned with Type 2 pitting, while papers from Germany are concerned with either or both types.

According to Mattsson [47] and in contrast to Campbell [9], three types of pitting of copper can be distinguished. These three types of pitting are also discussed in the review by Szklarska-Smialowska [48]. Type 1 occurs on annealed or half-hard tubes in cold tap water and is caused by a continuous carbon film formed during bright annealing at the inner tube surface. Type 2 occurs on hard-drawn tubes in hot tap water of low pH (<7.4) and a low $[HCO_3^-]:[SO_4^{2-}]$ ratio (<1). Type 3 occurs on hard, as well as annealed, tubes in cold tap water of high pH, with low salt concentration; this type of pitting is not caused by a continuous carbon film, and the reason for its formation is not yet known. Type 3 pitting was not discussed by Campbell [9].

4.1.1 Type 1 Pitting of Copper in Fresh Water

As discussed by Campbell [9] and Szklarska-Smialowska [48], Type 1 pitting of copper occurs in fresh waters having high concentrations of carbonate, sulfate, chloride, and organic colloids that serve as natural corrosion inhibitors. Furthermore, the presence of carbon films on the copper surface is necessary for Type 1 pitting. Such carbon films form from the thermal decomposition of organic lubricants used in tube-drawing operations.

Campbell [9] states:

> It was suggested in 1950 that one important reason why pitting corrosion of copper occurred in only a few localities in the United Kingdom was that most of the U.K. supply waters contained traces of "natural inhibitor" which prevent pitting corrosion of copper [49]. The evidence for this was published in two later papers [50, 51] and was summarized together with effects of other constituents in the water, by Campbell in 1964 [52]. According to this paper, the waters in which Type 1 pitting corrosion of copper occur are usually deep well supplies of high organic purity. River or lake waters do not give rise to pitting corrosion unless they have been treated to remove organic matter. This is because surface waters generally contain organic material which affects the form in which cuprous oxide is produced by the action of water on the copper. In its absence, the oxide forms as a loose, coarsely crystalline layer which affords no protection to the copper beneath but in its presence, the oxide forms an adherent layer which prevents further corrosion. The "organic inhibitor" responsible for this had not (and still has not) been isolated or identified but its nature had been investigated to some extent and tests for its presence developed. It had been shown to be a negatively charged colloidal substance with acidic properties, stable at temperatures up to 100°C (212°F) and capable of extraction from water by chloroform. It fluoresced whitish-blue in ultraviolet radiation and, on rather tentative interpretation of its infrared absorption spectrum, was thought possibly to be an unsaturated delta lactone.
>
> According to the same paper, the pH and temporary hardness of the water were less important than the presence or absence of organic inhibitor but affected the rate of pitting in waters free from inhibitor, low pH or moderately high temporary hardness favoring rapid attack since these conditions provide efficient cathodic depolarization [53]. Chlorides were considered essential for pitting to take place but the severity of attack was said not to vary much with chloride concentration within the normal range for supply waters.

Three tests for the organic inhibitor have been described [50, 51]. The first is a polarographic method in which a steadily increasing potential is applied between a dropping mercury cathode and a mercury pool anode in a cell containing the water under test, with sodium chloride added to give a total concentration of 200 ppm. Under these conditions, waters that cause pitting corrosion, or synthetic solutions to which no organic compounds have been added, give current-potential curves (polarograms) with a high peak in the step that represents the reduction of dissolved oxygen to hydrogen peroxide. Waters that do not cause pitting, and synthetic solutions to which negatively charged protective colloids have been added, give no peak or a very much reduced peak. The height of the peak can, therefore, be used as an inverse measure of the amount of organic protective colloids and hence usually of copper corrosion inhibitor in the water under test.

The second test depends upon the inhibitor's property of fluorescing pale blue in ultraviolet light. A fluorometer is used to compare the fluorescence of the water sample in ultraviolet light with that of a solution of sodium chloride in distilled water as a control. The intensity of the fluorescence is generally an indication of the concentration of inhibitor present.

The third test is more specific. It consists of passing a current of 10 microamps per square centimeter between two copper wire electrodes in a divided cell containing the water under test to which has been added 10% of a sodium chloride/sodium hydroxide solution of specified composition. The current is passed for 14 days and the presence or absence of inhibitor is deduced from the appearance of the oxide formed on the anode. Waters that do not contain inhibitor, and cause pitting, and synthetic solutions of similar composition, produce a coating of red crystalline cuprous oxide which flakes off easily when the electrode is bent, revealing a bright etched copper surface beneath. Waters that contain inhibitor, and do not cause pitting, form cuprous oxide on the anode as a dull brown, very adherent film which is unaffected by bending the electrode. If intermediate amounts of inhibitor are present, the anode is covered by areas of smooth "inhibited" oxide but with corrosion under patches of "uninhibited" oxide.

Devroey and Depommier [54], as a result of experiments in a large number of waters in Belgium and Luxembourg in which they related the action of the waters on copper to their calcium carbonate saturation index, their pH value, and their organic content as indicated by intensity of fluorescence in ultraviolet light, concluded that the waters that caused Type 1 pitting had a positive saturation index, pH value slightly above 7, and very slight or no fluorescence.

A survey recently conducted in the US indicated that pitting of copper plumbing tube in the US is almost invariably a cold water phenomenon associated with hard well waters. Based upon the conditions, it is assumed that the pitting is Type 1. It was reported [55, 56] that the waters involved contained over 5 ppm dissolved carbon dioxide, 89% containing between 10 and 40 ppm. The pH, however, lies typically within the range of 7.0 to 7.8; pH values below 7 reduce the tendency for pitting to occur. These waters also contained dissolved oxygen, in amounts up to 10 to 12 ppm, chloride, and sulfate. The sulfate level was generally about three to four times that of the chloride.

O. von Franque [57] found no pitting corrosion of copper in waters with less than 20 ppm chloride, but commented that copper tubes were successfully used with waters containing several hundred ppm. He found no relationship between pitting corrosion and free carbon dioxide content but observed that the incidence and type of pitting depended upon the sulfate content and carbonate hardness. Waters causing Type 1 pitting contained 40 to 400 ppm sulfate and 170 to 300 ppm carbonate hardness. Those causing Type 2 pitting contained 40 to 150 ppm sulfate, with less than 50 ppm carbonate hardness.

In the latest and most comprehensive investigation of the relationship between water composition and Type 1 pitting, Lucey [58] analyzed 17 waters, the behavior of which in relation to pitting corrosion of copper was well established, and produced a nomogram which related certain factors in their water analyses to the "pitting propensity" of the waters. The nomogram takes into account sulfate, chloride, nitrate, and sodium ion concentrations, dissolved oxygen concentration, and pH value. An increase in the sulfate or sodium ion concentration or in the dissolved oxygen

> concentration increases the pitting propensity of the water; an increase in the chloride or nitrate ion concentrations or in the pH value decreases the pitting propensity. Though Lucey's nomogram appears to be a valuable tool, it is important to note that it has no theoretical basis, nor even a basis of preconceived ideas about which constituents in water composition might be expected to affect pitting propensity.
>
> There is general agreement that Type 1 pitting corrosion is favored by a high sulfate content in the water and that failures occur most rapidly in waters of fairly low chloride content. Most authors associate Type 1 pitting corrosion with hard or moderately hard waters but it is notable that hardness is not one of the factors that affects the pitting propensity as calculated using Lucey's nomogram.

4.1.2 Type 2 Pitting of Copper in Fresh Water

This phenomenon is discussed by Campbell [9] and Szklarska-Smialowska [48]. The latter states:

> This type of pitting occurs in water with pH less than 7.4 and at temperatures above 60°C [42, 48]. Mattsson [47] found that pitting occurs in low pH water (generally 5 to 7) and that the water that causes pitting has a relatively low HCO_3^- content (up to 100 mg/l), while no pitting occurs in water with a higher HCO_3^- content (100 to 300 mg/l). The SO_4^{2-} concentration is 15 to 40 mg/l. At higher HCO_3^- concentrations, the protective basic copper carbonate forms. Mattsson [47] assumed that in carbonate-containing water (HCO_3^- = 15 to 70 mg/l with an SO_4^{2-} content > 0.2 gram-equivalent/l), a basic copper sulfate crust forms that covers the capillary mouth and thus creates an occluded cell at the anode where the following reaction can occur:
>
> $$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + e^- \qquad (1)$$
>
> As in Type 1 pitting, pits initiate below the metal surface deposit. Mattsson also found that in tubes with pitting, the inner tube wall generally had greenish-gray surface coating, often with a high aluminum content and some basic copper carbonate content; a green, basic copper sulfate crust covered the pits.

According to Campbell [9]:

> Rather less work has been done on the relationship between Type 2 pitting and water composition, but there is a fair measure of agreement on the subject. Levelton [59] quotes a typical analysis of waters causing Type 2 pitting corrosion in the Canadian North Pacific Coast area as pH 6.3, total solids 25.2 ppm, total hardness 4.2 ppm, total alkalinity 3.5 ppm, dissolved oxygen 10.9 ppm, free carbon dioxide 1.5 to 4.5 ppm. Mattsson and Fredriksson [60] have reported that in Sweden, Type 2 pitting occurs in waters with pH less than 7.4 and a ratio of bicarbonate to sulfate less than unity. This accords with the experience of von Franque in Germany [57], and Gilbert [61] has reported that it also applies to cases reported in the UK.
>
> The variety of Type 2 pitting involving deposition of manganese dioxide requires, of course, the presence of manganese in the water but trouble has been experienced with waters containing as little as 0.03 ppm. The waters concerned are soft moorland-derived supplies but, unlike the waters associated with normal Type 2 pitting, have usually been treated to raise the pH well above 7.

4.1.3 Types 1 and 2 Pitting of Copper in Seawater

According to Campbell [9]:

> Copper can suffer Type 1 pitting corrosion in seawater but the pits that form tend to be very wide in relation to their depth and the rate of penetration is consequently less than in fresh waters. Pitting can be caused by carbon films, as in fresh waters, but it can be produced also by sulfide contamination of the seawater, for example, by sewage in harbors and river estuaries. Seawater containing small amounts of sulfide tends to form a sulfide film on copper instead of the usual cuprous oxide film and this more readily breaks down to produce pitting. Type 2 pitting in seawater has not been reported, even at high temperature and low pH.

4.2 Effect of Surface Condition

According to Campbell [9]:

The surface condition of the copper tube as manufactured appears to have no influence on the incidence of Type 2 pitting but there is abundant evidence that it is of vital importance in Type 1 pitting. Attention was first drawn to this factor by work at the British Nonferrous Metals Research Association (BNF) in 1949 and 1950 [62]. It was found that a high proportion of copper water pipes that failed by Type 1 pitting corrosion contained carbon deposits. Out of a total of 80 pitted tubes, 62 contained more than 1.9 mg/dm^2 of carbon and only 7 had less than 1.0 mg/dm^2, while out of 13 unpitted pipes from service in the same district, one contained 1.0 mg/dm^2 of carbon but all the rest had less than 1.0 mg/dm. Carbon deposits were attributed to breakdown of drawing lubricant residues during bright annealing of the (half hard) tubes in manufacture. The pitted tubes containing less than 1.0 mg/dm^2 of carbon contained a thin film of cuprous oxide scale that is formed on copper by annealing under slightly oxidizing conditions, and it was suggested that the carbon films and the glassy cuprous oxide scales were both formed during annealing in the course of manufacture and that both stimulated pitting corrosion by providing a large surface which was cathodic to the copper beneath.

Later, the BNF ceased to use the weight of carbon deposit per unit area as a reliable indication of the presence of dangerous carbon films and adopted a test in which any carbon film present in a tube sample is detached by immersion in 25% nitric acid and observed with a low power binocular microscope. Tubes from service containing glassy cuprous oxide scale were found to have very thin carbon films on top of the oxide, suggesting that the oxide could not have been formed during annealing as originally suggested. Simulated service tests of copper tubes with very thin carbon films in them confirmed that the glassy cuprous oxide developed beneath the carbon during service and was not, therefore, a primary cause of pitting corrosion.

Further evidence indicating the dangerous character of carbon films, the harmless character of glassy cuprous oxide films formed during annealing, and the effect of very thin carbon films in encouraging development of shiny cuprous oxide in service, as well as encouraging pitting was provided by service trials carried out in Belgium by Devroey and Depommier in 1960–1961 [54]. These researchers also developed a semi-quantitative test for carbon films in copper tubes. In this test, carbon is detached from the copper tube sample by treatment with nitric acid, hydrofluoric acid is added to dissolve siliceous matter, the insoluble residue is filtered off under specified conditions, and the filter paper then compared visually with standards prepared using carbon black. The results are expressed on a logarithmic scale ranging from zero (no carbon present) to 8. This V.T.R. Carbon Black Test has, in the past few years, been adopted in many laboratories and has shown good correlation between Carbon Black Number and liability to pitting corrosion, but there is disagreement on the maximum Carbon Black Number that can be tolerated in tubes if they are to have high resistance to pitting corrosion. This difference of opinion probably arises principally from differences in the standards used by various laboratories due to differences in the particle size and blackness of the carbon black used to prepare the standards.

The importance of carbon films in causing Type 1 pitting corrosion is now widely recognized, for example, in Germany [57], New Zealand [63], Holland [64], Denmark [65], and Iceland [66]. The national standards for copper tube in the UK and in New Zealand require the tubes to be "clean and free from deleterious films in the bore"and a recent draft German standard [67] lays down a test for carbon films similar to that used in Campbell's original work [49]. Copper tube manufacturers in the UK, Belgium and Germany adopt special procedures (usually abrasive cleaning) to remove any carbon films that might be formed during manufacture, the introduction of this treatment producing a dramatic reduction in the number of failures of copper water pipes by pitting corrosion [68, 69].

Copper tubes in which oxide films have been produced during annealing may show enhanced resistance to pitting corrosion, possibly because the oxidizing conditions in the annealing furnace would burn off any lubricant residue that might otherwise break down to form carbon films. In their first series of field trials, Devroey and

Depommier [54] found that tubes containing oxide films formed by annealing in a slightly oxidizing atmosphere showed a clear advantage over tubes that had been bright annealed. In their second series of tests, however, the performance of tubes containing oxide films was variable and they concluded that such films could not be relied upon to protect copper tubes from pitting corrosion. Two series of service trials in The Netherlands, one lasting for 3 years and the other for 4-1/2 years, both led to the conclusion that the presence of cuprous oxide films, found in the tubes during annealing, gave a significant degree of protection, especially to tough-pitch copper [64]. Some hot formed oxides can, however, stimulate pitting corrosion. Heavy oxide layers formed during extensive brazing operations usually consist of a thin layer of cupric oxide with cuprous oxide underneath. Such scales are highly cathodic to copper and can give rise to pitting corrosion at the boundary between the scaled and unscaled parts of the metal surface.

According to Szklarska-Smialowska [48]:

Frommeyer [70] studied the composition of corrosion products formed on copper during Type 1 pitting by electron spectroscopic methods. The concentration profiles of different elements in the film are shown in Fig. [2]. The author found via Electron Spectroscopy Chemical Analysis (ESCA) that carbon does not occur in the carbonate form of copper or calcium, but derives from the

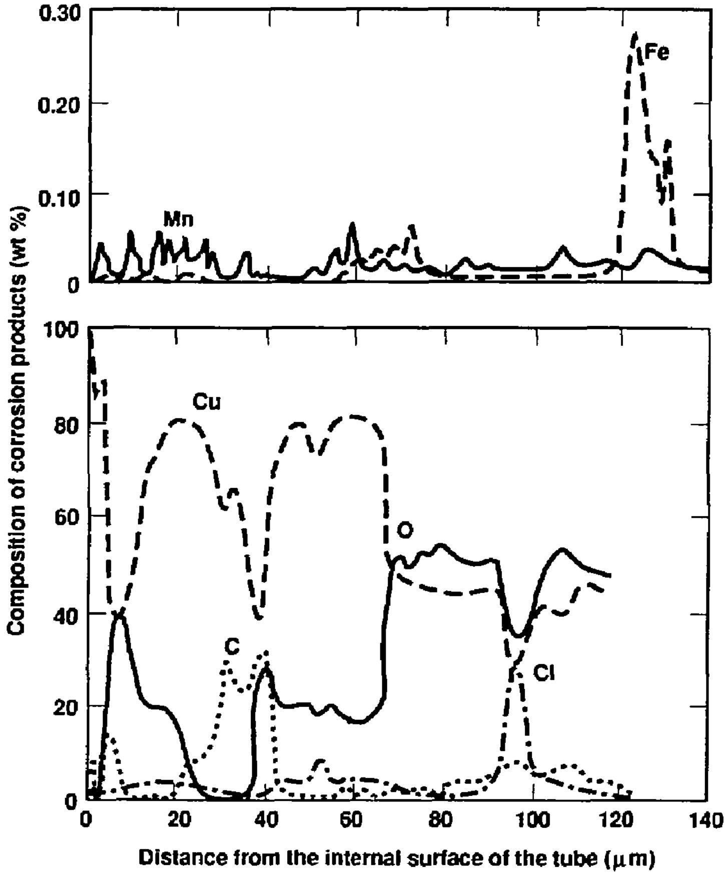

Figure 2. Concentration profiles of copper, oxygen, chlorine, iron, and manganese on copper [70].

lubricants. The absence of Mn and Fe in region 1 (below Cu_2O membrane) is thought to indicate that carbon only deposited on copper is responsible for pitting.

Because of the detrimental effect of deposited carbon, a particular procedure is often used to remove carbon films that form during tube manufacture. Abrasive cleaning is normally used.

Carbon residue on copper, however, is insufficient to produce pitting. Studying the influence of various degrees of carbon contamination in the bore, Cornwell et al. [71] found that the electrode potential never exceeded the pitting potential in water that did not support pitting, even when high carbon contamination was present. On the other hand, when the tube specimen contaminated by carbon was immersed in aggressive water, it underwent pitting, but specimens abrasively cleaned did not pit. In the last case, the electrode did not reach the pitting potential.

4.3 Effect of Composition

According to Szklarska-Smialowska [48], "it was found by Cornwell et al. [71], that copper containing approximately 1% tin or aluminum (particularly tin) is more resistant to pitting in the presence of carbon residues than ordinary commercial copper."

According to Campbell [9]:

> Tough-pitch and deoxidized arsenical and nonarsenical coppers are used in water supply and all are liable to suffer pitting corrosion under unfavorable circumstances. They do, however, differ slightly in their susceptibility. Devroey and Depommier found in field trials [72] that phosphorus-deoxidized copper was slightly more resistant than electrolytic tough-pitch copper to pitting corrosion, and Gerth [73] has reported a high incidence of pitting corrosion in tough-pitch copper tubes used in certain areas of Germany where phosphorus-deoxidized tubes have given relatively little trouble. Recently completed 4-1/2 year service trials in ten towns in The Netherlands showed [64] arsenical phosphorus-deoxidized copper tubes to be slightly more susceptible, and tough-pitch copper tubes much more susceptible to pitting corrosion than nonarsenical phosphorus-deoxidized copper.

4.4 Effect of Temper

According to Campbell [9]:

> Copper water pipes are used in the fully soft, half-hard or hard-drawn conditions. Any effect of temper on corrosion resistance is, to some extent, inevitably associated with effects of surface condition arising from differences in manufacturing procedure. For example, the incidence of Type 1 pitting in hard-drawn tubes is low, but since the probability of there being carbon films in tubes supplied in the hard-drawn condition is small, this may simply reflect their freedom from carbon films. Devroey and Depommier [72] however, made a detailed comparison of phosphorus-deoxidized copper tubes of different temper all containing sufficient carbon to give a V.T.R. Carbon Black Number of 4–6. The tubes were tested for 1 year in a pitting water supply at Haren and the results are shown in Table 2.

Table 2. Effect of temper on pitting-corrosion susceptibility performance in tests at V.T.R., Haren (phosphorus deionized tubes with Carbon Black Numbers of 4 to 6).

Temper	Number of tubes	Maximum depth of pitting after 1 yr		
		<0.1 mm	0.1–0.45 mm	>0.45 mm
Soft	13	3 (23.1%)	2 (15.4%)	8 (61.5%)
Half-hard	62	41 (66%)	13 (21%)	8 (13%)
Hard	33	33 (100%)	0	0

4.5 Fundamental Aspects of Pitting

This section discusses the fundamentals of pitting, beginning with an overview of conceptual mechanisms in Sec. 4.5.1. An appreciation for the role of various environmental species in the localized attack of copper can be gained from reading Sec. 4.5.1. This is followed by a discussion of the thermodynamic stability, growth kinetics, and morphology of passive films on copper (Sec. 4.5.2 and 4.5.3). Finally, a discussion of the critical pitting potential, the potential required for localized breakdown of the passive film, is presented in Sec. 4.5.4.

4.5.1 Mechanism of Copper Pitting

According to Szklarska-Smialowska [48]:

> Two points of view exist concerning pitting of copper. One postulates that on the surface of copper, oxygen reduction occurs on a large cathodic area, and pitting occurs on a small anodic area [74–76]. The other view [77, 78] presumes that oxygen reduction occurs above the pit, not on the surrounding area. Pitting is thought to occur when a cuprous chloride pocket forms below a porous, electrically conductive membrane that permits CuCl to diffuse through it. This membrane separates the anode from the cathode. It is suggested that pits initiate where CuCl formation occurs. Local accumulation of corrosion products, resulting from general (uniform) attack on the copper surface, is thought to produce pitting.
>
> Cornwell et al. [79], suggested the following chemistry is involved in the pitting of copper in aerated supply waters:
>
> $$Cu^+ + Cl^- \rightarrow CuCl \qquad (2)$$
>
> CuCl hydrolyzes to form cuprous oxide, which is precipitated on the metal surface:
>
> $$2CuCl + H_2O \rightarrow Cu_2O + 2HCl \qquad (3)$$
>
> The cathodic reaction supporting the anodic dissolution process is oxygen reduction:
>
> $$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (4)$$
>
> For corrosion to proceed, the hydroxyl ions produced at the cathodic sites must be removed. This occurs more readily in acid supply water or water that contains bicarbonate ions:
>
> $$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O \qquad (5)$$
>
> The last reaction causes precipitation of mixed calcium carbonate and basic copper carbonate scale.

Iron can also have a significant influence on the pitting of copper. According to Szklarska-Smialowska [48]:

> Kristiansen [80] studied pitting of copper in distilled water containing 10 mg SO_4^{2-} and 5 mg CO_2/l with and without an iron ion addition, at temperatures of 45°, 50° and 60°C. In aerated neutral water, iron is present in Fe^{3+} form. Ferric ions are reduced according to the following reaction when deposited on copper surface:
>
> $$Fe^{3+} + Cu \rightarrow Cu^+ + Fe^{2+} \qquad (6)$$
>
> Ferrous ions are again oxidized to Fe^{3+}, causing further copper corrosion. The author [80] was able to establish, using radioactive ^{59}Fe, that pits nucleated where iron was present on the metal surface. It was also found that the highest corrosion occurred at 50°C, which was explained by the decomposition of the basic copper carbonate deposit and formation of a more protective copper oxide at higher temperatures. However, pits were also found on copper when no iron had been added, but the presence of iron in the water could not be excluded.

Szklarska-Smialowska [48] explains that the effect of carbon is explained differently by Lucey [77, 78] and Pourbaix [81]. In Lucey's theory, the effect of carbon is attributed to the increased production rate of primary corrosion products, and to the hindering of the CuCl diffusion from the pit. According to Pourbaix, copper coupled with carbon increases corrosion potential to values at which copper pitting occurs. The same effect would be obtained by coupling copper to a more noble metal.

According to Campbell [9]:

> The first detailed study of the mechanism of Type 1 pitting corrosion of copper was carried out by May [75], who stressed the importance of the role of solid cuprous chloride within the pit. This, he considered, acted as a highly efficient oxygen screen, preventing access of oxygen from the water

to the anodic region at the bottom of the pit, and also acted as an anodic depolarizer, keeping the copper ion concentration low because of its low solubility. May also discussed various ways in which pits might be initiated by local breakdown or blistering of normally protective oxide films on the copper surface or as a result of differential aeration cells set up by deposits. Campbell [51] endorsed May's views and suggested that carbon films in the tube provided large effective cathodic areas round the anodic areas (probably at cracks in the carbon film) where pitting occurs. He discussed also the reduction of dissolved oxygen at the cathodic areas and the possible rate-controlling effects of carbon dioxide and calcium bicarbonate, both of which act as cathodic depolarizers by removing hydroxyl ions formed by reduction of oxygen.

More recent studies of the mechanism of Type 1 pitting have been carried out by Pourbaix and his colleagues [82–86]. They have studied the thermodynamic equilibria for copper in chloride, bicarbonate and mixed chloride/bicarbonate solutions, and have prepared potential/pH diagrams for these systems and for Brussels tap water. These Pourbaix diagrams will be discussed in greater detail in a subsequent section. They agree with May's view of the importance of the formation of cuprous chloride in pitting corrosion of copper but consider that it hydrolyzes to form cuprous oxide and hydrochloric acid, thus producing within the pit a solution of low pH. They suggest that pitting corrosion in copper is due to the formation of cuprous chloride as a metastable primary corrosion product which hydrolyzes at the surface of the metal if there are local conditions that restrict diffusion, for example, under a deposit of malachite and cuprous oxide or under a calcareous deposit. These conditions give rise to local formation of a solution of pH 2.5 to 4.0 containing cuprous oxide. In such an environment, the copper within the pit will dissolve if its electrode potential is above a critical value in the neighborhood of +20 to +77 mV, SCE.

The electrode potential within a pit is different from the overall potential of the copper specimen, but the two are interdependent. According to Pourbaix, copper suffers no corrosion at all in Brussels water if its overall potential is below -250 mV, SCE. At potentials between -250 and +25 mV, SCE, it develops a protective oxide film but suffers no significant corrosion. If its potential settles between +25 and +150 mV, SCE, as it usually does, a certain amount of general corrosion occurs, but nothing of a serious nature. Pitting corrosion occurs only when, as a result of exceptional circumstances, the general electrode potential raises to values above about +170 mV, SCE. Such potentials can be reached by coupling the copper to a more noble metal or to carbon.

Pourbaix et al. [82] also studied the changes in potential with time that occur when copper is immersed in Brussels tap water and have discussed the effects of illumination on these potentials. During the first 10 or 15 days after immersion, the potential of the copper rises from about -30 to 0 mV, SCE, and illumination has no effect on the electrode potential. During the next fortnight, the potential continues to rise to about 50 mV, SCE, and malachite forms on top of the cuprous oxide. After 20 to 30 days, sudden falls in potential occur as a result of local breakdown of the protective films. When this stage is reached, illumination of the metal surface produces an immediate fall of potential to about -240 mV, SCE, from a normal potential of 50 to 100 mV, SCE. This marked photoelectric effect is considered to be due to photochemically stimulated dissociation of cuprous chloride to produce metallic copper. Illumination can play no part in the development of pitting corrosion of copper water pipes, but the development of photoelectric properties in the film forming on the copper during immersion in Brussels tap water is interesting because it indicates a change in the nature of the film and probably the development of cuprous chloride in the film. Similar observations have been made independently by Lucey [77, 78] who interprets them in a rather similar manner.

Lucey published a theory of pitting corrosion of copper in 1967 [77, 78] based on detailed examination of service failures and extensive laboratory experiments. All the previous discussions of pitting corrosion had postulated a large cathodic area surrounding the small anodic region at which pitting was taking place. The production of hydroxyl ions by the reduction of oxygen at the cathodic area should, in hard waters, result in precipitation of a calcium carbonate scale on the cathodic surface. Lucey found, however, on examining a large number of examples of pitting corrosion of copper pipes and tanks from hard water districts, that there was no more carbonate scale deposited around the pits than on other parts of the surface quite remote from any pitting. There was, however, a large amount of calcium carbonate present in the mound immediately above the pit. This suggested that the reduction of dissolved oxygen in the water takes place imme*diately above* the pit and *not on* the surrounding surface.

He also showed that a cuprous oxide membrane is present across the mouth of the pit and demonstrated that this acts as a thin bipolar membrane electrode, the under surface acting anodically and the upper surface cathodically. Cuprous chloride produced within the pit is anodically oxidized to cupric on the under surface of the oxide membrane, and the cupric ions thus produced can attack further copper within the pit to reform cuprous ions. The principal cathodic process occurring on the upper surface of the oxide membrane is the reduction of cupric ions formed from cuprous ions by reaction with dissolved oxygen in the water. The cuprous ions for this reaction are provided partly by diffusion through pores in the oxide membrane from within the pit and partly by recycling of the cuprous ions produced by cathodic reduction at the upper surface of the membrane. A mound forms above the pit consisting partly of basic cupric salts and partly of calcium carbonate formed by reaction between the cuprous ions, oxygen and calcium bicarbonate. Figure [3] is a diagrammatic representation of the structure of a corrosion pit in copper, and indicates the nature and site of each of the reactions involved.

Lucey's theory is revolutionary in rejecting the classical small-anode-surrounded-by-a-large-cathode model of pitting and placing the anodic and cathodic process on the lower and upper sides of an oxide membrane above the area where corrosion is occurring. It is of interest, therefore, that Evans has recently suggested [87] a possible electrochemical mechanism of atmospheric rusting that is in some respects similar to Lucey's mechanism of pitting of copper. Evans postulates a layer of magnetite, containing ferrous sulfate in the pores, above the area where rusting is taking place,

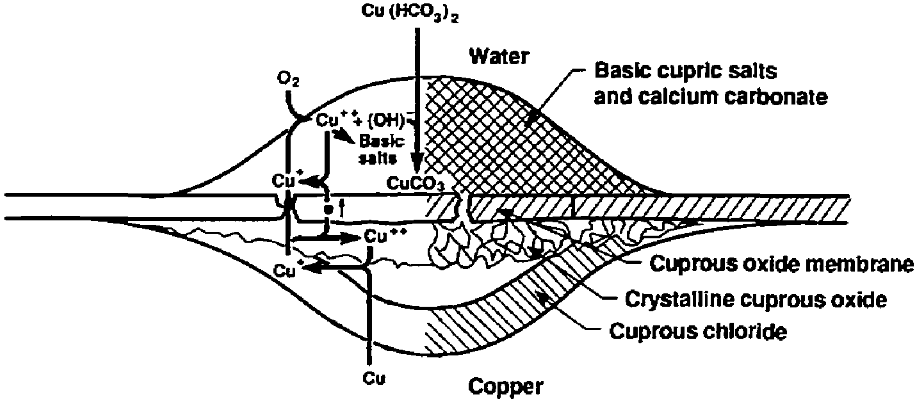

Figure 3. Representation of the arrangement of corrosion products and of the reactions involved in the pitting corrosion of copper [77, 78]. (a) Reaction occurring within the mound above a pit: $4CuCl + Ca(HCO_3)_2 + O_2 \rightarrow CuCO_3 \cdot Cu(OH)_2 + CaCO_3 + 2CuCl_2$. (b) Cathodic electrode reaction occurring on the outer surface of the oxide membrane: $Cu^{2+} + e^- \rightarrow Cu^+$. (c) Anodic electrode reaction occurring on the inner surface of the oxide membrane: $Cu^+ - e^- \rightarrow Cu^{2+}$. (d) Reaction between the anodic product and the copper within the pit: $Cu + Cu^{2+} \rightarrow 2Cu^+$.

and suggests that the anodic attack on the iron beneath this membrane is balanced by cathodic reduction of ferric rust to magnetite on its top surface, the ferric rust being reformed by atmospheric reoxidation of the newly formed magnetite. Lucey's theory of pitting of copper and Evans' theory of atmospheric rusting both require ability of the metal to form a porous electronically conducting oxide membrane and to exist as ions in solution in two states of oxidation, the lower state being easily converted to the higher by atmospheric oxygen. Probably few metals other than copper and iron meet both these requirements.

Lucey's papers deal with the initiation of pitting corrosion as well as with the mechanism that maintains an established pit. He considered the essential step in the development of a corrosion pit in copper to be the formation of a cuprous oxide membrane that is sufficiently porous to permit cuprous chloride to diffuse through it, has sufficiently high electronic conductivity to act as a bipolar electrode, and is locally separated from the underlying copper by a small pocket of solid cuprous chloride. When clean copper is immersed in water, slight general corrosion occurs, producing, primarily, cuprous chloride at local anodic spots. Some of this is lost by diffusion into the bulk of the water, some by formation of basic cupric salts, and some by hydrolysis to cuprous oxide. The result is normally the development of a protective film of cuprous oxide and basic copper salts. Pitting will only occur if the conditions at any particular spot accelerate the formation of cuprous chloride or decrease the rate at which it is removed by formation of basic salts, hydrolysis to oxide, or diffusion into the water. Only then will solid cuprous oxide be formed beneath an oxide membrane.

Lucey's studies of the distribution of pitting corrosion in copper tanks and hot water cylinders and his laboratory experiments showed that local accumulation of the primary products of general corrosion of a copper surface can produce pitting. A stream of soluble, or possibly colloidal, primary corrosion products formed by slight general corrosion of copper can cause pitting to occur on a copper surface placed where these corrosion products can accumulate. The primary corrosion products have been shown to have a strong cathodic depolarizing action and are believed, therefore, to contain copper in the cupric state, but their composition has not been fully elucidated. They are believed to stimulate pitting, partly by direct reaction with the copper to produce cuprous chloride and partly by providing a supply of cupric ions for reduction at the outer surface of oxide membrane cells that would otherwise probably be too small to be self-sustaining.

Pitting corrosion is, therefore, encouraged by circumstances that increase the production of streaming primary corrosion products or increase the probability of their collecting in any particular spot. It would be discouraged by conditions that altered the character of the primary corrosion products or tended to disperse them into the water, and pitting will not occur if local production of cuprous chloride can be suppressed or its rate of formation is less than the rate of loss by hydrolysis, diffusion, etc. Carbon films are now believed to cause pitting by increasing the rate of production of primary corrosion products and by providing a screen through which cuprous chloride can diffuse away only slowly. They probably also provide a support on which a cuprous oxide membrane can build up and can, during the early stages of the development of a pit, act as a bipolar electrode in place of the cuprous oxide membrane. Films of inert material such as lacquers and nonconducting metal soap films formed during drawing or rolling can also act as diffusion screens and as supports for oxide membrane formation and thus encourage development of pitting. They would be less effective than carbon films since they cannot cause galvanic acceleration of the initial general corrosion or act directly as membrane electrodes while the oxide membrane is forming.

Lucey studied the effects of time and of illumination on the potential of acid-pickled copper immersed in water. In waters that support pitting corrosion, the potential rises rapidly from an initial value of about -250 mV, SCE, to about -165 mV, SCE, and then more slowly, reaching -50 mV, SCE, after about 2 days, and usually settling at about 0 mV, SCE, after approximately 3 days. Similar potential-time curves are given by copper in waters that contain natural inhibitor and do not support pitting corrosion, and the films formed in the two types of water appear similar, but they behave differently on illumination. Films formed in waters that do not support pitting corrosion show no change in potential, or a small change in the positive direction, on illumination. Films formed in waters that support pitting corrosion behave in a similar manner during the very early stages of film growth (while the potential is below about -150 mV, SCE), but in the later stages become photonegative, i.e., the potential moves sharply in the negative direction on illumination.

Lucey suggests that the reason for the difference in photoelectric behavior of the two apparently similar types of cuprous oxide films is that the photonegative oxide has small pockets of solid cuprous chloride present beneath its surface, i.e., it contains incipient corrosion pits and is, therefore, potentially dangerous. A cuprous oxide film on copper would normally show a small positive shift of potential on illumination because the oxide is a p-type semiconductor, but the cuprous chloride, being an n-type semiconductor, produces a negative shift. Using the photonegative behavior of potentially dangerous oxide films as a means of recognizing them, Lucey showed that this type of oxide film forms on a horizontal copper surface, in water that can support pitting corrosion, if it is subjected to the action of a stream of primary corrosion products formed by slight general corrosion of copper turnings in a glass tube supported above it. If, however, the potential of the horizontal specimen is artificially held below the minimum of -150 mV, SCE, at which the potentially dangerous type of oxide can form, the protective type is formed even under these conditions.

This observation led to the use of aluminum sacrificial anodes to hold the potential of copper water tanks and cylinders below -150 mV, SCE, during their first few months of exposure to water. By the time that the aluminum has corroded away, the protective type of film has formed on the copper, and subsequent freedom from pitting corrosion is ensured. During the past 5 years, aluminum anodes termed "protector rods" have been fitted extensively in copper hot water cylinders and tanks in districts in the UK where pitting corrosion of these was previously a serious problem, and no case has yet been reported of a tank or cylinder fitted with a protector rod failing by pitting corrosion [88].

There appear, at first sight, to be staggeringly wide differences between the potentials reported by Pourbaix and his colleagues for copper in Brussels water and those reported by Lucey. Other potential measurements on copper tube samples exposed to a hard pitting water have been made at Bramham, Yorkshire, by Gilbert [89], with results similar to those of Pourbaix. All the tubes tested by Gilbert gave a potential of about 0 mV, SCE, on first immersion. Those that were clean internally settled after about 10 weeks to potentials below 100 mV, SCE, and did not develop pitting, but tubes containing carbon films settled to potentials above 170 mV, SCE, and developed Type 1 corrosion pits.

The differences between the potentials reported by Lucey on the one hand and by Pourbaix and Gilbert on the other are probably explained by the fact that Lucey used acid-pickled copper samples in short term tests, whereas Pourbaix and Gilbert both used commercially produced copper tube in much longer term tests. A link between Gilbert's observations and Lucey's is provided by recent unpublished observations by Lucey. He had previously shown that the photonegative, potentially dangerous type of cuprous oxide does not form at potentials below -150 mV, SCE; he subsequently found that photopositive, protective type of oxide is unstable at potentials above 60 mV, SCE. This implies that freedom from pitting should be experienced only if the potential of the copper with its water formed film is below 60 mV, SCE, a value not very different from the 100 mV, SCE, quoted by Gilbert.

Lucey's ideas on the initiation and general mechanism of pitting corrosion in copper explain many of the features of Type 1 pitting that are experienced in practice. For example, the tendency for pitting to occur preferentially along the bottom of horizontal tubes and in the base of copper tanks is sometimes taken to indicate that the pitting is initiated by deposits settling out from the water, although no evidence is usually found of such deposits being associated with the particular points where pitting has occurred. According to Lucey's theory, however, pitting would be expected to occur preferentially at such points since they are where primary corrosion products will tend to accumulate. The lower incidence of Type 1 pitting in hot waters than in cold is explained by the greater rate of diffusion of primary corrosion products away from the copper surface and the greater rate of hydrolysis of cuprous chloride at the higher temperature.

Lucey's theories do not provide any explanation of the effects of water composition on pitting corrosion of copper. The potential-pH diagrams produced by Pourbaix for copper in Brussels tap water and in dilute solutions of chloride and bicarbonate provide some theoretical basis linking water composition and pitting corrosion, but considerable discretion is required in applying them to waters of different composition, since small changes in the composition of the solution can produce very big changes in the potential-pH diagram.

Since the development of photoelectric activity, indicative of the formation of cuprous chloride, was preceded by formation of malachite in Pourbaix's experiments with copper immersed in Brussels water [82], he and his colleagues have studied in some detail the conditions of formation of malachite on copper from solutions containing sodium bicarbonate [86]. Polarization experiments in which the potential of a copper electrode was varied at a slow constant rate indicated that 0.001 to 0.003*M* solutions of sodium bicarbonate were slightly corrosive, and 0.01 to 0.03*M* solutions highly corrosive. The concentration range 0.01 to 0.03*M* corresponds to the conditions of stability of malachite, which can form a protective deposit on the metal and so suppress corrosion, but which can also produce pitting corrosion if chloride is present.

The effects of corrosion products on pitting corrosion of copper have also been discussed and studied by Mattsson and Fredriksson [60], but with particular reference to Type 2 pitting. They used an "artificial pit" cell in which a copper wire anode coated with a polymer was inserted into a glass capillary tube which extended slightly beyond the end of the copper wire. The screened anode thus formed was placed, together with a large copper cathode, in a vessel containing the test solution at a temperature of 75°C (167°F); a constant voltage of 0.5 V was applied and the current recorded. The effects of varying the pH and bicarbonate, sulfate and chloride content of the test solution on the current flowing in the cell and on the nature and composition of any corrosion product precipitated was studied.

At pH 6, with chloride or sulfate present, no insoluble corrosion products formed; the corrosion current was comparatively high and remained constant throughout the 4-day test. Waters of pH 7–9 formed green corrosion product "crusts" which were of three types. Type I formed in the glass capillary tube close to the copper anode in all waters containing bicarbonate but free from sulfate and chloride; the amount formed was insufficient for X-ray diffraction analysis. Type II formed just outside the mouth of the capillary tube in all waters containing 10 ppm of sulfate or more, except when the bicarbonate content was high (280 ppm), and was shown by X-ray diffraction analysis to consist of basic copper sulfate. Type III formed inside the capillary, but away from the copper anode, in all waters containing chloride and in waters containing sulfate together with 280 ppm bicarbonate; the amount formed was insufficient for analysis. Current-time curves corresponding to the formation of the three types of crust, and to the case where no crust formed, are shown in the reference. It is clear that the conditions causing greatest corrosion of the anode in the artificial pit cell were those that resulted in formation of the Type II crust.

It was pointed out many years ago by Evans that solid corrosion products can be protective or harmful according to whether they are formed in immediate contact with corroding metal (Mattsson's Type I crust) or at a sufficient distance from the metal surface to provide a screen between the corroding metal and the surrounding solution (Type II crust). The latter situation permits the establishment of local highly corrosive conditions beneath a slightly porous cap of corrosion products. Linking the work of Mattsson, Lucey and Pourbaix, this can be interpreted as meaning that the water compositions that produced Type II crusts in Mattsson's experiments would provide conditions for the hydrolysis to produce local acidity, and so establish a corrosion pit.

4.5.2 Thermodynamic Stability of Passive Films on Copper

As discussed in Vol. 4, in 1976 Marcel Pourbaix was selected as the Palladium Award Medalist of the Electrochemical Society [90–92].

During his address he reviewed much of his work on predicting potential-pH diagrams for copper and copper-based alloys. Much of his work in this field was motivated by the International Copper Research Association (INCRA). This organization asked Pourbaix to elucidate some fundamental electrochemical aspects of the pitting corrosion of copper tubes in cold water, which was a severe problem in the United States and several European countries such as Belgium, Germany, The Netherlands, and the United Kingdom during the early 1960s.

Several diagrams relevant to the repository environment at Yucca Mountain are presented by Pourbaix [90]. Figure 4 represents the equilibria for the Cu-H_2O system at 25°C and shows regions of immunity, free corrosion, and passivation. The passive film is either Cu_2O (cuprite), CuO (tenorite), or hydrated Cu_2O_3, depending on potential and pH. Note that cuprite or cuprous oxide, Cu_2O, forms at the most anodic potentials, near the free corrosion potential. Figure 5 shows the potential-pH diagram for the ternary system Cu-Cl-H_2O, for solutions containing 355 ppm Cl^-. Note that Well J-13 water contains approximately 10 ppm Cl^-. In cases involving chloride, there are acidic regions where films of $3Cu(OH)_2 \cdot CuCl_2$ or CuCl form in addition to the oxides of copper.

The effect of CO_2 and SO_2 on the Pourbaix diagram for copper in chloride-containing water is illustrated in Fig. 6. Figure 6 is for the quinary system Cu-Cl-CO_2-SO_3-H_2O, at 25°C for solutions containing 229 ppm CO_2, 46 ppm SO_3, and 22 ppm Cl. Note that these compositions are similar to those found in the water in Brussels. Furthermore, the stable form of copper in the presence of oxygenated Brussels water (pH of 8) is known to be $CuCO_3 \cdot Cu(OH)_2$, malachite, which is consistent with Pourbaix's calculations. In addition to cuprite, malachite, tenorite, and Cu_2O_3, Pourbaix's calculations predict CuCl (nanterite) and $CuSO_4 \cdot n\, Cu(OH)_2$, where n can be either 2 or 3 (antlerite and brochantite, respectively) in acidic regions. In the absence of oxygen, the stable form of copper in Brussels water is Cu_2O. Cuprous chloride, CuCl, is unstable under these conditions, and thus tends to be hydrolyzed, with formation of Cu_2O and HCl.

The Pourbaix diagrams for the ternary system Cu-CO_2-H_2O at 25°C, are shown in the original reference and in Vol. 4 of the *Survey of Degradation Modes* (UCID-21362 Vol. 4). Calculations were done assuming various CO_2 concentrations from 44 to 44×10^3 ppm. In addition to cuprite, tenorite, and Cu_2O_3, one could expect the formation of species such as $nCuCO_3 \cdot Cu(OH)_2$, where n can be either 1 or 2 (malachite or azurite, respectively) in slightly acidic or slightly alkaline environments. The Pourbaix diagram for the ternary system Cu-SO_3-H_2O, at 25°C for 46 ppm dissolved SO_3, is also shown. The oxides of copper tend to form in alkaline solutions, while cuprite, brochantite, antlerite, or Cu_2O_3 form in acidic solutions, depending on potential. In acidic media and at practical potentials, copper dissolves as either Cu^+ or Cu^{2+}. In contrast, the species responsible for dissolution in alkaline media is probably CuO_2^-.

Angus and Angus have developed a new computational approach for generation of Pourbaix diagrams using the concept of virtual species [93]. Computation of the equilibrium composition in complex was accomplished by treating the active element as a virtual species. For ideal solutions, the equation set can be solved sequentially, rather than simultaneously, for the concentrations of all species. For nonideal solutions, the method provides the basis for an efficient iterative solution. The procedure gives a simple test for phase stability and an algorithm for defining the boundaries of the regions of dominance of the dissolved species, which is independent of concentration. Unfortunately, the virtual species approach is restricted to systems involving only one redox element, M, and to pure solid phases containing only M, H, and O. No other solids (such as carbonates or chloride complexes) were considered, though it is possible to do so. Angus and Angus calculated several potential-pH diagrams for the Cu-H_2O system, each for a different total concentration of dissolved copper (10^{-8}, 10^{-6}, and 1*M*). These diagrams compare favorably with those calculated by Pourbaix for the Cu-H_2O system.

4.5.3 Experimental Studies of Oxide Films on Copper in Other Environments

As discussed in Vol. 4, Topham and Miller [94] studied the anodic oxidation of copper single crystals in 0.05*N* solutions of $Cu(ClO_4)_2$ and $Cu(CHO_2)_2$, having pH values of about 4.2 and temperatures of about 30°C. They found that islands (polyhedra) of Cu_2O form on copper single crystals in both $Cu(ClO_4)_2$ and $CuSO_4$ solutions. The islands grow laterally until the surface is

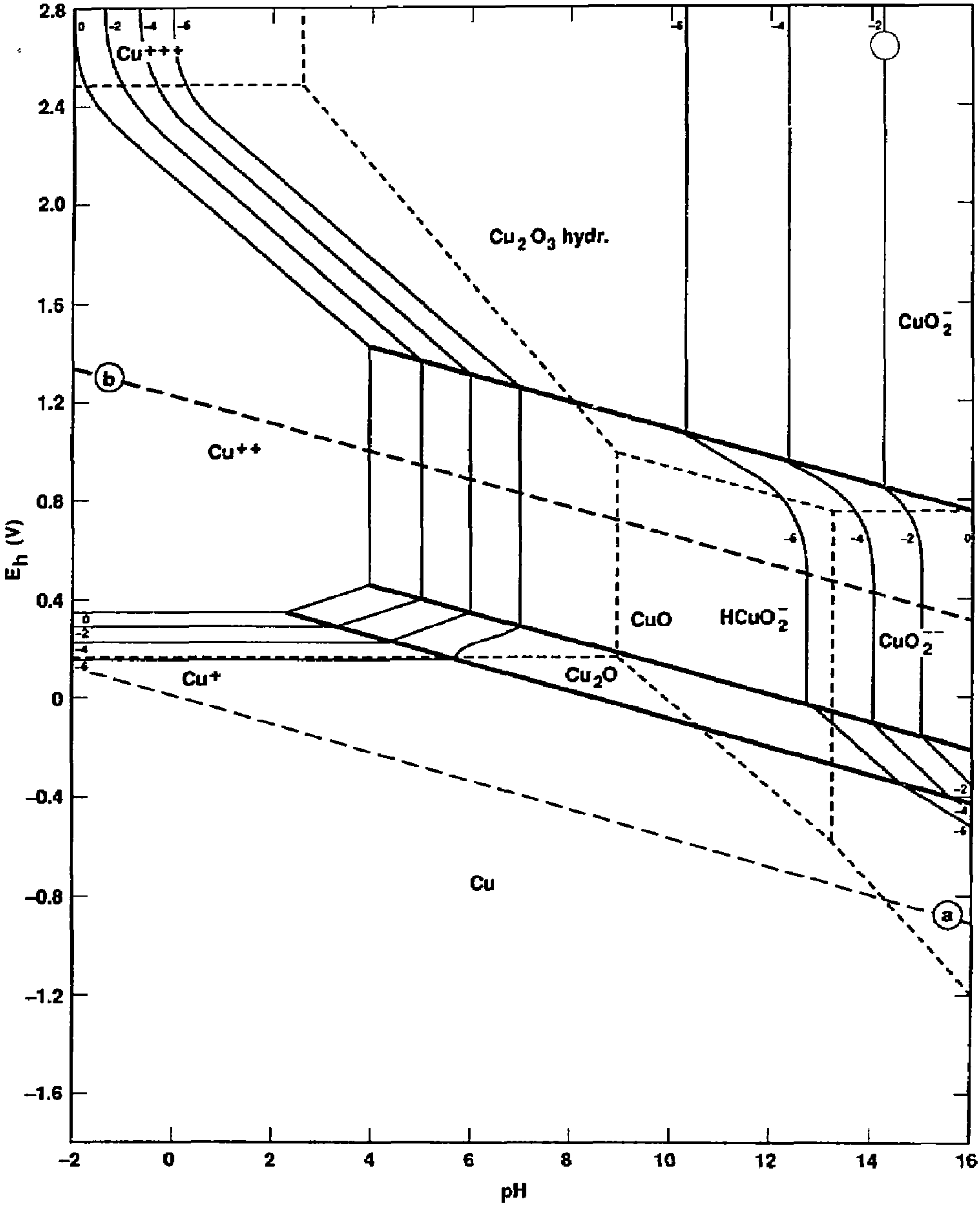

Figure 4. Potential-pH equilibrium diagram for the copper-water system at 25°C [90].

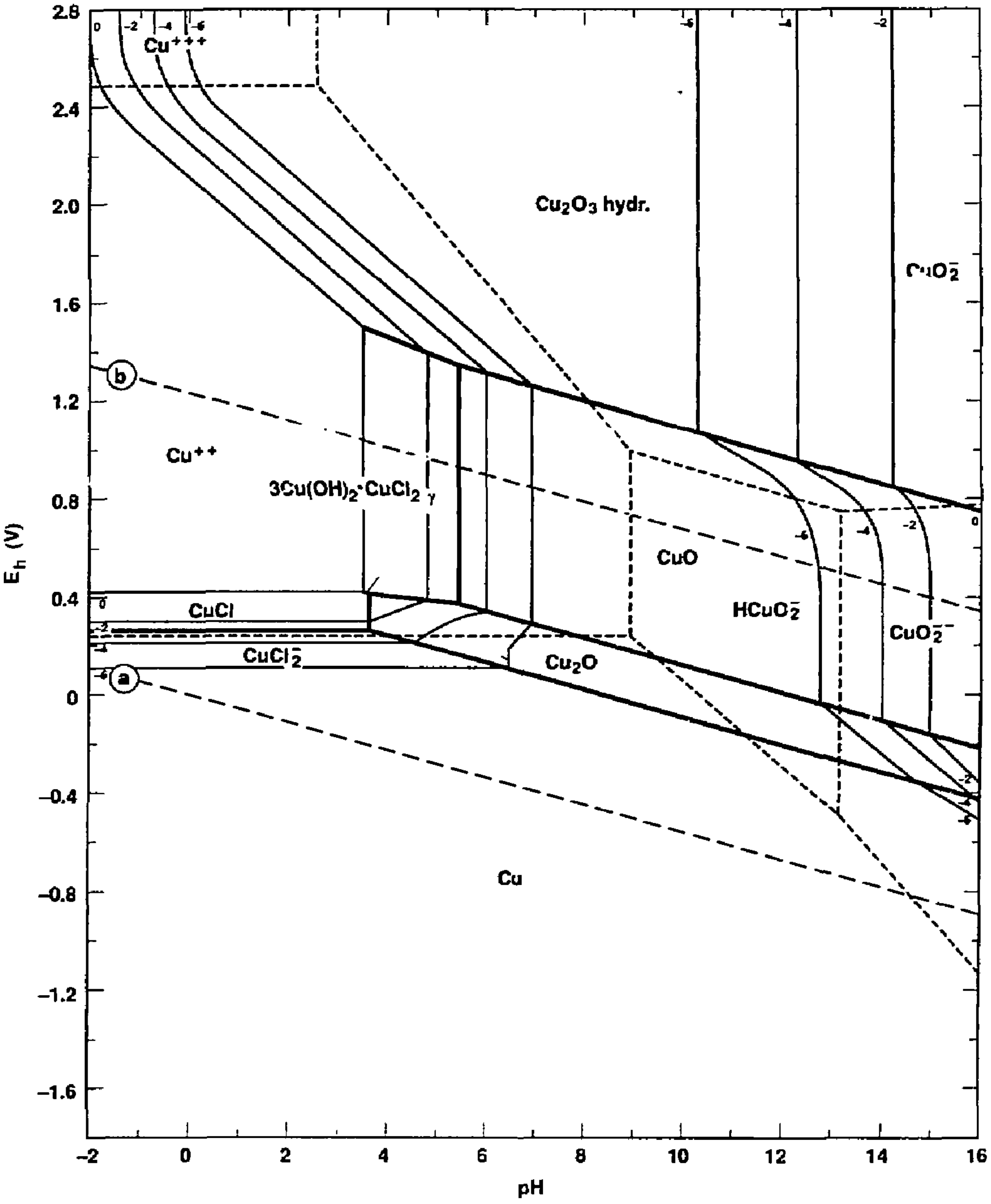

Figure 5. Potential-pH equilibrium diagram for the three-component system Cu-Cl-H_2O, for solutions containing 355 ppm Cl^- (10^{-2} g · ion/liter) [90].

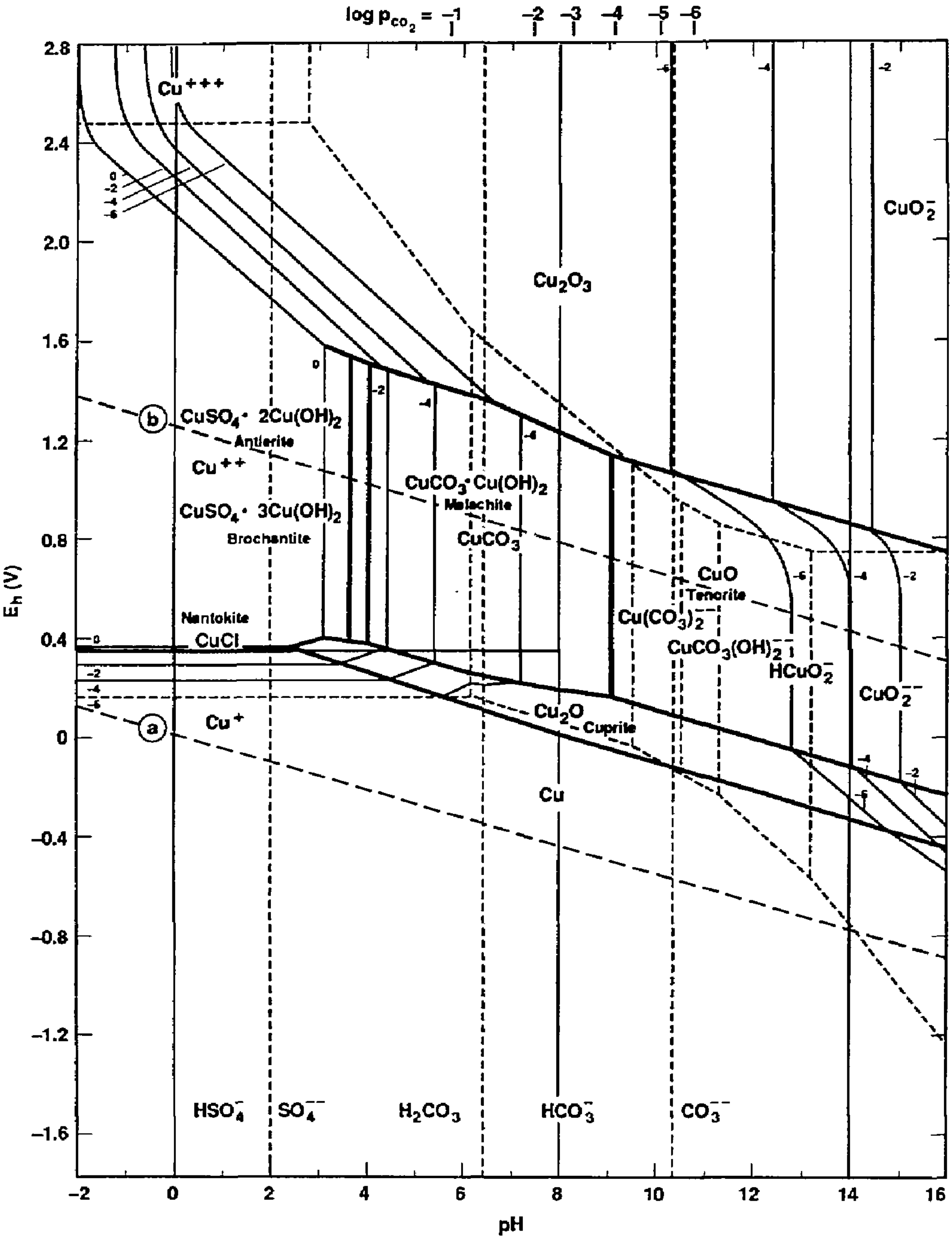

Figure 6. Potential-pH equilibrium diagram for the system Cu-Cl-CO_2-SO_3-H_2O, at 25°C (for solutions containing 22 ppm Cl^-, 229 ppm CO_2, 46 ppm SO_3) [90].

completely covered with oxide. The lateral growth rate is greater in perchlorate solutions than in sulfate solutions. Cu_2O films that form in $Cu(CHO_2)_2$ solutions on the (110) and (111) faces of copper single crystals are smooth and continuous, whereas islands (polyhedra) form on the (100) face.

Porterfield and Miller report the growth kinetics of these films in a separate paper [95]. They found that oxide growth on the (100) face occurs by an apparently uniform mechanism over an extended period of time. The mathematical form of the growth law is roughly parabolic: $\log L = (1/n)\log t + \text{constant}$, where L is the film thickness, t is time, and n is 1.86. Such behavior is expected in systems where the drift velocity of cationic holes limits film growth. The drift velocity is proportional to electric field strength, which decreases as L increases. Film growth on the (110) face is quite different. Initially, the growth rate is greater on the (110) face than on the (100) face, as reflected in the value of n (1.57). However, after a few minutes, growth slows dramatically and almost stops. Growth on the (111) face follows the parabolic law ($n = 1.99$) for a few minutes, and then slows. Growth eventually accelerates. The authors believe that differences in growth rate (values of n) observed on the different crystal faces might be due to corresponding differences in film morphology.

4.5.4 Critical Potential for Localized Breakdown of Passive Film

As discussed by Szklarska-Smialowska [48]:

> Pourbaix [81] first determined pitting potential of copper during Type 1 pitting. The values measured in Brussels, Belgium, tap water were approximately 170 mV, SCE, for the concave internal surface of copper tubes and approximately 100 mV, SCE, for the surface of copper wires. These potentials were only slightly higher than the equilibrium potential of $Cu/CuCl/Cu_2O$ measured inside pits (24 mV, SCE). Inside pits, the solution contained 207 ppm Cl^- and 17 ppm copper, pH 3.4. Other investigators [96, 97] confirmed the existence of a critical potential for pitting of copper.
>
> Pourbaix [98] observed that the potential of copper specimens immersed in flowing Brussels water shifted in the positive direction during exposure. Three stages were differentiated. During Stage 1, following immersion, the potential is relatively low (−30 to −10 mV, SCE); the metal is covered with a red Cu_2O deposit, and HCl forms as a result of CuCl hydrolysis. During Stage 2, potential increases (−10 to +50 mV, SCE). Greenish malachite appears and acidification of the solution inside the starting cavity occurs. Stage 3 is characterized by the same processes as Stage 2; potential continues to increase irregularly, and pits develop. When equilibrium conditions within the pit have been established, stable CuCl forms on the pit bottom.

As discussed in Szklarska-Smialowska [48], Thomas and Tiller have performed detailed polarization experiments to determine the critical pitting potential of surface films on copper [99]. Szklarska-Smialowska states: "Figure [7] gives three examples of anodic polarization curves in NaCl solutions. The breakdown potential is lower, the higher the NaCl concentration. In 1M NaCl, the pitting potential is not well defined. When the specimen is immersed for a long period of time in dilute NaCl solution, the pitting potential is not observed, and general corrosion occurs." It is important to note that this conclusion may be inconsistent with those of Lucey, which were discussed by Campbell. See Sec. 4.1.1 above. Lucey concluded that Na^+ may promote pitting, but that Cl^- probably inhibits pitting. Lucey's conclusions are inconsistent with common knowledge as well as with the work of Thomas and Tiller.

Szklarska-Smialowska [48] continues by stating:

> In the presence of other halogen anions in NaCl, copper pitting is inhibited, but the I^- action differs from that of Br^- [100]. In iodides, inhibition is caused by the formation of a CuI layer on the metal surface, while KBr acts by reducing the solution's oxygen content. In very dilute KBr solutions, however, copper corrosion increases.
>
> Three examples of anodic polarization curves for copper in $NaHCO_3$ solutions are shown in Fig. [8] [Ref. 44]. With increasing $NaHCO_3$ concentration, the oxide layer's protectiveness toward general corrosion decreases, which is probably caused by increasing soluble copper carbonate complex formation. However, increasing HCO_3^- concentration increases the oxide layer stability toward breakdown. It is assumed [44]

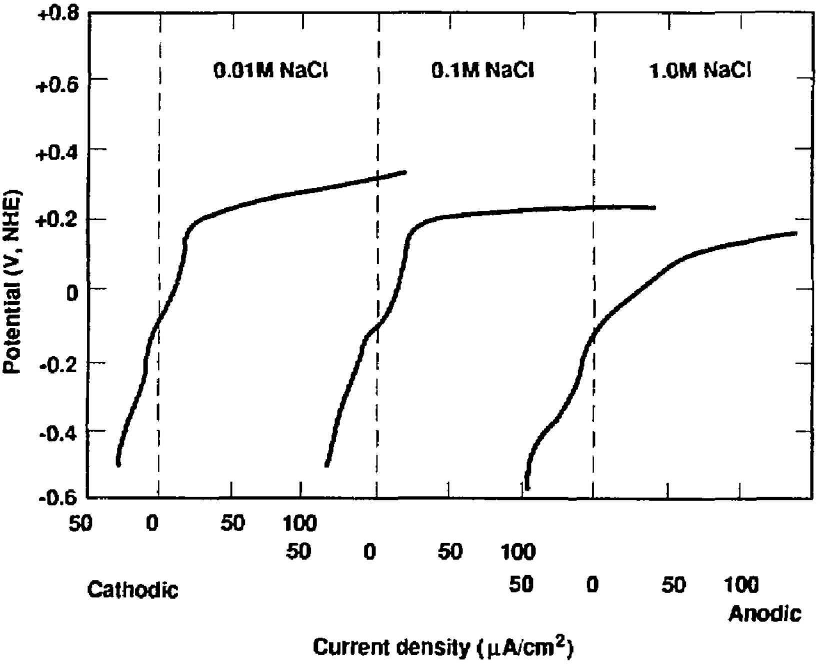

Figure 7. Potentiokinetic polarization curves for copper in NaCl solutions at 25°C; scan rate 40 mV/min [99].

that breakdown occurs through interaction of HCO_3^- with cupric hydroxide film. As the temperature increases from 25 to 90°C, the oxide film is less protective, and the pitting potential shifts to less positive values.

Thomas and Tiller [101] have published a second paper on the formation and breakdown of surface films in sodium bicarbonate and sodium chloride solutions. They paid particular attention to the effects of pH and temperature. The anodic behavior of copper in air-saturated solutions at 25, 60, and 90°C has been determined by stepwise potentiostatic polarization. In 0.01*M* $NaHCO_3$, the critical breakdown potential of the protective oxide layer is displaced to considerably more positive potentials as the temperature increases. In 0.01*M* $NaHCO_3$ containing 0.01*M* NaCl, the critical breakdown potential is displaced to more negative values with increasing temperature, but the corrosion potential-breakdown potential difference undergoes little change. In 0.01*M* NaCl, the surface film on copper is essentially nonprotective, and linear Tafel plots are observed. A change in the pH of 0.01*M* $NaHCO_3$, with or without 0.01*M* NaCl, from 8.6 to 7.3 has little effect on the values of the breakdown potentials.

Fujii et al. [102, 103] have attempted laboratory reproduction of pitting on copper in a hot, circulating water loop for the purpose of clarifying the mechanism and establishing countermeasures to the pitting. Type 2 pitting was observed to occur on the internal surface of copper tubes after long-time exposure to Tokyo water when heated to 60°C and residual chlorine of 2 to 3 mg/l was added. After prolonged loop testing, the electrode potential of copper exceeded the critical value, +150 mV, SCE. The pits were deep and acute and were covered with greenish-blue products, which were identified as basic copper sulfate. Pitting did not occur in water free of residual chlorine even under

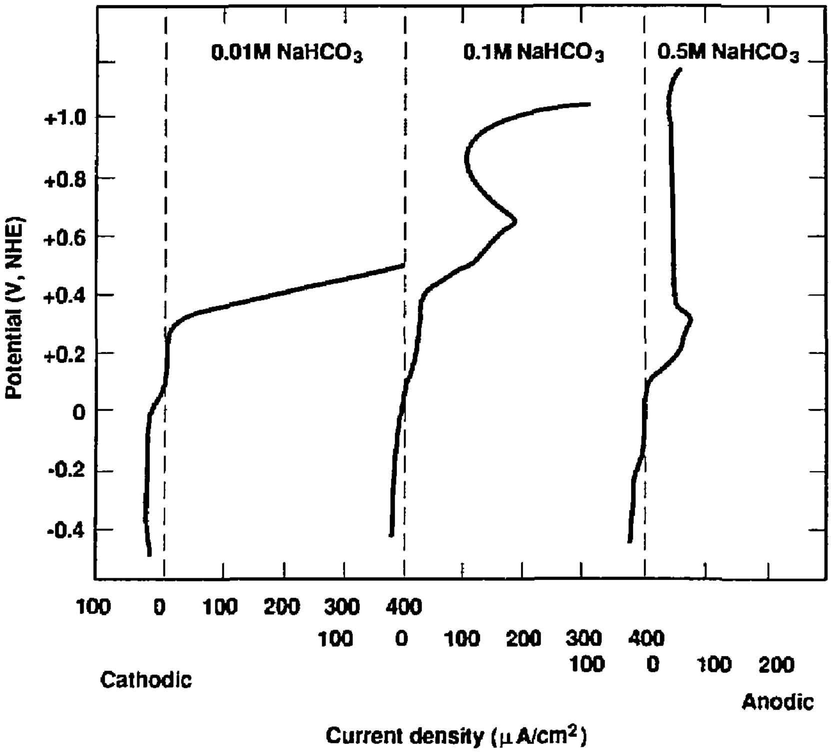

Figure 8. Potentiokinetic polarization curves for copper in $NaHCO_3$ solutions at 25°C; scan rate 40 mV/min [99].

air-saturated conditions, in which copper retained a low potential value.

Joseph et al. [104] have studied the pitting of copper tubing in drinking water. They concluded that the danger of pitting corrosion in hard drawn copper tubes by drinking water (pH of 7.8, 168 ppm Cl^-, 256 ppm SO_4^{2-}, 215 ppm $CaCO_3$, etc.) was not appreciable because of the slowness of formation and reaction of the solid corrosion products. For samples of copper tubes not covered partially or completely by carbon films, potential-time curves show an initial period during which they reached their highest potentials, not exceeding 506 mV, NHE (265 mV, SCE), and after that, a secondary period in which the voltage slowly increased with frequent brisk drops, which could be explained by cracks developing in the film.

5. Pitting of Copper-Based Alloys

5.1 Pitting of Aluminum Bronze

According to Campbell [9]:

> Binary aluminum bronzes containing more than about 9% aluminum are liable to a form of selective attack similar to dezincification and known as "dealuminification" if this occurs locally, it can be considered a specialized form of pitting. It occurs only if the material has been cooled slowly through the temperature range 900 to 400°C (1652 to 752°F) with resultant partial breakdown of the corrosion resistant beta

phase to the gamma-2 phase. Pitting corrosion similar to Type 1 pitting corrosion of copper can affect other aluminum bronzes, including the complex alloys containing iron and nickel. The presence of sulfide in the water or of graphite mold dressing residues are possible causes of the trouble.

5.2 Pitting of Cupronickel Alloy

Campbell states [9]:

> The copper nickel alloys in most common use are 70/30 cupronickel (Cu-30Ni, CDA 717, British Standard designation CN 102). Iron is added to both alloys to impart high resistance to corrosion-erosion in seawater (0.5% in the 30% nickel alloy and 1.5% in the 10% nickel alloy). These iron additions improve the film forming ability of the material in seawater and, within limits, the greater the iron content, the more protective the film that is formed. If, however, the iron content is too high, the film is liable to blister, and pitting corrosion develops beneath the blisters. According to Bailey [105], the resistance of 70/30 cupronickel (Cu-30Ni) to corrosion by moving aerated seawater is greatly increased by the presence of 0.3 to 1% iron, but, if the iron content exceeds 1%, the alloy shows a tendency to local pitting at shielded areas. Consequently, British Standards for 70/30 cupronickel set the maximum iron content at 1%. Opinion in the US generally puts the iron content at which 70/30 cupronickels become liable to pitting corrosion rather lower, and US specifications for Alloy 717 give a maximum iron content of 0.7%. It should be noted, however, that a copper-nickel condenser tube alloy containing 30% nickel with 2% each of iron and manganese has been widely used for very many years and does not show any particular susceptibility to pitting corrosion in service.
>
> The 90/10 cupronickel alloy (Cu-10Ni) is generally considered to be more resistant to pitting corrosion than the 70/30 alloy. This is partly because, since it forms a somewhat less protective film, any pits that do develop tend to be broader and not so deep. Marine organisms such as barnacles and weed are liable to attach themselves to the surface of 70/30 cupronickel (Cu-30Ni), and most other materials, if the velocity of the seawater at the metal surface is below about 3 feet per second. The points of attachment of the organisms to the metal are particularly liable to pitting corrosion, since organisms act as an oxygen screen and their metabolism may produce corrosive substances such as organic sulfur compounds and amino acids. The higher rate of general corrosion of 90/10 cupronickel (Cu-10Ni) and the consequent presence of copper ions (which are toxic to most marine organisms) at its surface gives this alloy a high resistance to fouling and associated pitting corrosion.

Osborn and Sudrabin [106] have given some quantitative data on pit depths observed in Cu-30Ni (CDA 715) in seawater. For example, after 12 months of exposure to quiescent seawater, the uniform depth of corrosion ranged from 0.2 to 0.9 mil/yr, whereas the depth of localized attack ranged from nil to 6 mil/yr (at crevice). Similar results were observed at a flow rate of 2 ft/s. There was negligible localized attack at 10 and 15 ft/s; however, there was substantial impingement attack (111 mil at 15 ft/s). Because of the importance of impingement attack in marine heat exchangers, significant quantitative data exist for this type of corrosion. For example, Francis has studied the effect of chlorine and sulfide on impingement attack of condenser tubes [107–109]. His data are not relevant to the repository conditions.

5.3 Thermodynamic Stability of Passive Films on Copper-Based Alloys

As discussed in Vol. 4, Pourbaix diagrams have not been found for copper-aluminum and copper-nickel alloys; however, it is informative to study the diagrams for aluminum and nickel presented in Pourbaix's *Atlas of Electrochemical Equilibria in Aqueous Solutions* [110]. At pH values greater than 2, aluminum is passivated with a film of hydrargillite, $Al_2O_3 \cdot H_2O$, at all potentials within the thermodynamic limits of water. In acidic media having a pH less than 2, aluminum dissolves as Al^{3+}. Similar behavior would be expected for aluminum bronze. The surface would probably become passivated with hydrargillite, rather than cuprite, due to the difference in the free energies of formation. The unusual stability of this passive film is responsible for the relatively low uniform oxidation and corrosion rates observed for aluminum bronze. In the case of nickel, the surface would probably be passivated with $Ni(OH)_2$, Ni_3O_4, Ni_2O_3, or NiO_2, depending upon potential and pH. Though Pourbaix diagrams for copper-nickel and copper-aluminum alloys have not been predicted, Candela and Chang have presented a technique for predicting such diagrams for alloys in the gas phase [111].

5.4 Experimental Studies of Films on Aluminum Bronze and Cupronickel Alloys

As discussed in Vol. 4, McGuire et al. have used Auger spectroscopy to perform *ex situ* analysis of passive films formed on Cu-30Ni in chloride solutions [112]. They concluded that these passive films are composed primarily of nickel oxide. Misra and Burstein have used various electrochemical techniques, including the scratch test and linear polarization, to study the behavior of freshly generated electrode surfaces of nickel, Ni-30Cu, Ni-50Cu, and Ni-70Cu (similar to CDA 715) in 1*M* H_2SO_4 [113]. They believe that film formation at low potentials begins with a monolayer of CuOH and/or NiOH. At high potentials, passivation of the alloys is believed to be due to film growth under high electric field, with two different sets of high-field parameters for different film thicknesses. Under these circumstances, the expression for film growth rate, expressed as the anodic current transient, $i(t)$, is given as

$$\log i(t) = \log A + [(BzFp)(E - E_g)/2.3M\, q(t)] \quad (7)$$

where A and B are constants (high-field parameters), z is the charge number of the cation, F is Faraday's constant, p is the film density, M is the molecular weight, E_g is the equilibrium potential for film formation, $E - E_g$ is the potential drop across the film, and $q(t)$ is the cumulative charge density involved in film formation at time t. The rate of film growth for all alloys is controlled largely by the nickel oxide component of the film.

5.5 Pitting Due to Dealloying

As discussed in Sec. 5.1, localized dealloying of alloy surfaces can result in pitting. Consequently, it is important to develop an understanding of this mode of degradation in copper-based alloys. As discussed in Vol. 4, Pryor and Fistor have studied the mechanisms and kinetics of dealloying of copper solid solutions and intermetallic phases [114]. Potentiostatic experiments in 0.5*N* NaCl at -0.25 V, SCE, showed that the kinetics of dealloying of copper-based binary alloys fall in the following order: Cu-Al > Cu-Mn > Cu-Zn > Cu-Ni. The copper-nickel alloys are less susceptible to dealloying than the copper-aluminum alloys. The kinetics of dealloying of the copper-aluminum alloys obey the following relationship:

$$\log S_\varepsilon = KC_s \quad (8)$$

where S_ε is the excess solute concentration (mg/cm^2/20 hr) dissolved from the alloy, and C_s is the atom percent of solute in the alloy. K is related qualitatively to the reversible potential of the solute element. The authors concluded that the kinetics of dealloying are primarily controlled by electrochemical factors and not by solid state diffusion. The rate of dealloying of copper-nickel was several orders of magnitude less than that of copper-aluminum, and was so small that a kinetic expression could not be developed from the data.

As discussed in Vol. 4, Lennox and Peterson have studied the corrosion and dealloying of copper-aluminum and copper-nickel alloys in seawater [115]. They found that copper-aluminum alloys such as CDA 612 and 614 (similar to CDA 613) are susceptible to dealloying. However, dealloying could be prevented by cathodic protection. In contrast, copper-nickel alloys such as CDA 706 and CDA 715 are essentially immune to dealloying.

Ferrara and Caton have studied the dealloying of cast aluminum and nickel-aluminum bronzes in seawater [116]. They concluded that dealloying in duplex-phase aluminum bronze castings is a significant problem and is often undetectable by visual inspection. Dealloying depths in excess of 13 mm have been observed in some castings. More recently, Tuthill has reviewed literature on the application of copper-based alloys in seawater service [13]. He also cited the work of Ferrara and Caton and noted that dealuminification of aluminum bronzes is not a significant problem until the aluminum content reaches the 9- to 11-at.% range. This may be due to the formation of new alloy phases. Tuthill stated that denickelification occurs occasionally in overhead condensers with high nickel content used in refineries where hydrocarbon streams condense at temperatures above 149°C. Gleekman and Swandby have documented the massive dealuminification and failure of aluminum bronze rotating drums used to dry $CaCO_3$ pastes having pH values of approximately 8 [117]. Minor impurities of Cl^- and SO_4^{2-} in the paste were found to significantly enhance the rate of dealuminification.

6. Crevice Corrosion of Copper and Copper-Based Alloys

According to France [118]:

> Crevice corrosion is a form of localized attack that occurs at shielded areas on metal surfaces exposed to certain environments. The sites for this type of corrosion often are unavoidable because of the structural or functional design and may even arise during the exposure period. Examples include spot-welded lap joints, threaded or riveted connections, gasket fittings, porous welds, valve seats, coiled or stacked sheet metal, marine or debris deposits, and the meniscus at a water line.
>
> The penetration of corrosive solutions into these relatively inaccessible areas, with widths that are typically a few thousandths of an inch, can result in various types of failures: the metal surface may become stained or perforated by the corrosive; the mechanical strength may be reduced below tolerance limits so that fracture occurs from the applied load or from the wedging action of the corrosion products; operating components may seize; or protective coatings may be disbonded from the metal surface.

There is little doubt that corrosion in crevices is a complex process that involves several competitive and synergistic factors that have been investigated and discussed by several researchers, including Rosenfeld and Marshakov [119].

6.1 Mechanisms of Crevice Corrosion

France states [118]:

> Much of the theoretical interpretation of crevice corrosion has been associated with some sort of concentration cell. This concept is based on the fact that the initiation and propagation of localized attack on metal surfaces is influenced by nonuniformity of the corrosive solution. For example, variations in the concentration of ions or dissolved gases may arise along the same metal surface because of the existence of crevices that are relatively inaccessible to fresh electrolyte compared with freely exposed surfaces. Such environmental conditions cause potential differences and influence electrode kinetics to the extent that an electrochemical cell is established, wherein an oxidation process (that is, corrosion) occurs at the anodic sites, and some reduction process (for example, oxygen reduction) occurs at the cathodic sites.

Vermilyea and Tedmon [120] developed a simple theory for the concentration and variation of potential in a crevice and compared predictions with experimental data. A consequence of the theory, confirmed by experiments, is that a small difference in potential in a crevice can cause a large change in concentration and a corresponding large increase in corrosion current at a given applied potential. The theory gives a simple way to estimate concentrations in crevices in real situations.

6.1.1 Metal-Ion Concentration Cell

According to France [118]:

> This mechanism is based on the development of differences in metal-ion concentration between the inside and outside of a crevice. Laboratory experiments with an electrochemical cell consisting of two short-circuited copper electrodes, each immersed in a different concentration of copper sulfate solution in electrical contact through a porous barrier, have shown that corrosion occurs predominantly in the solution with the low metal-ion concentration. From the

Nernst equation, the electromotive force (emf) of such a divided cell with a $1 \times 10^{-4} N$ solution in the anode chamber and a $1N$ solution in the cathode chamber is 130 mV. By analogy, such a cell can be formed in practice after the metal ions formed by the initial corrosion reactions accumulate within the crevice where solution flow or diffusion is restricted. Once a difference in metal-ion concentration is established, accelerated dissolution (that is, $M \rightarrow M^+ + e^-$) is anticipated at anodes just outside the crevice, whereas the reduction of metal ions (that is, $M^+ + e^- \rightarrow M$) is anticipated at the cathodes within the crevice. A schematic representation of the operation of this crevice cell is illustrated in Fig. [9(a)].

6.1.2 Differential Aeration Cell

According to France [118], this mechanism depends on the occurrence of different dissolved oxygen concentrations in the solution adjacent to a metal surface. In a crevice situation, the oxygen is replenished more easily on the exterior surfaces than within the shielded crevice, where corrosion is accelerated as the result of oxygen depletion. See Fig. 9(b).

6.1.3 Active-Passive Cell

France states [118]:

> This cell is sometimes considered to be another example of differential aeration, but it deserves special attention; the depletion of

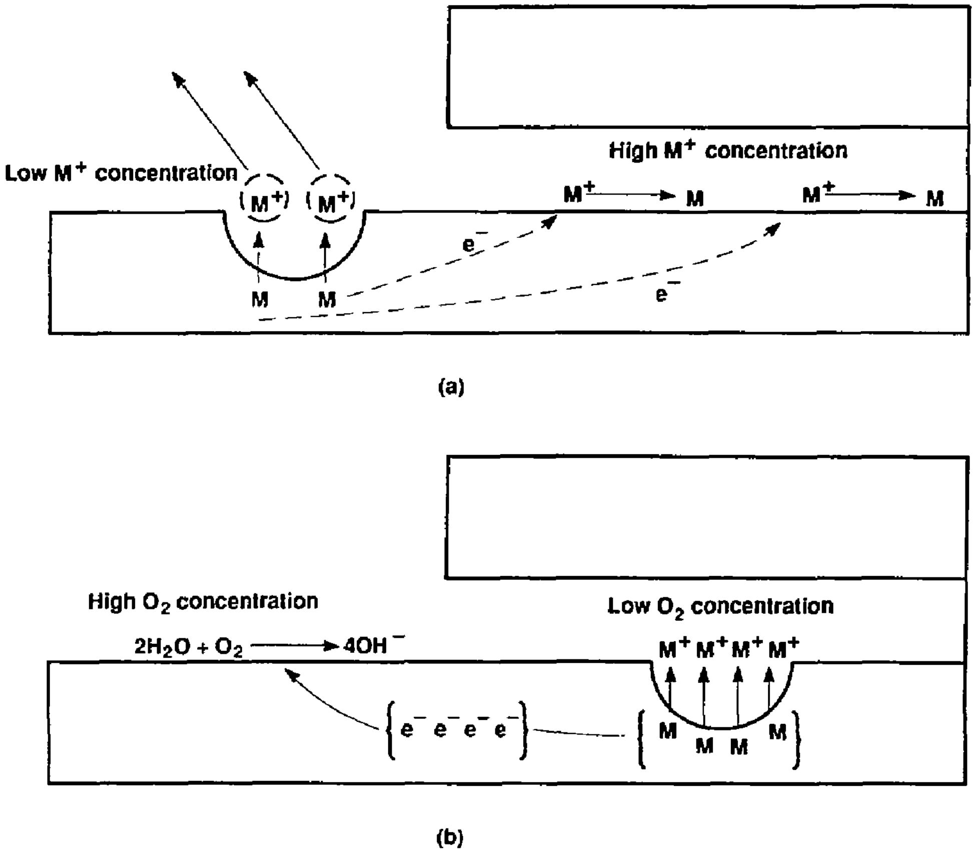

Figure 9. Schematic representation of crevice corrosion mechanisms [118]. (a) Metal-ion cell. (b) Differential aeration.

any oxidizer in a crevice can initiate localized attack on active-passive metals because the establishment and maintenance of passivity depends upon the availability of sufficient oxidizer concentrations. Therefore, a deficiency of oxygen can prevent the reformation of protective oxide films at damaged areas on a metal surface, which become active and corrode at an accelerated rate.

As shown in Fig. [10(a)], the anodic oxidation process is dependent on the effectiveness of the reduction process. For example, reduction process A would promote active metal dissolution. In contrast, process C would promote passivity of the metal. Such a graphical presentation facilitates the understanding of crevice corrosion, especially for active-passive cells, but the conclusion related to corrosion at active potentials may be misleading if the anodic interior and cathodic exterior areas of the crevice are considered a corrosion couple. For example, with the oxidation-reduction reactions shown in Fig. [10(b)], the corrosion current inside the crevice (i'_{in}) is greater than that outside the crevice (i'_{out}) at the corrosion potential of the couple ($E'_{couple(in/out)}$), and crevice corrosion would be predicted. However, it is evident that in the uncoupled state, the exterior is corroding at a faster rate (i'_{out}) than the interior (i'_{in}) of the crevice.

Equation (9) defines the length of an active-passive crevice that can be passivated, and Eq. (10) defines the length of a passivated crevice that can be maintained passive [121].

$$L_p = E_p \sqrt{W/(\rho i_c \Delta E_a)} \quad \text{(active-passive)} \quad (9)$$

and

$$L_p = \sqrt{(W \Delta E_p)/(\rho i_p)} \quad \text{(passive)} \quad (10)$$

where L_p is the passive length, ΔE_p is the passive potential range, W is the crevice width, ρ is the solution resistivity, i_c is the critical anodic current density, i_p is the passive current density, and E_a is the active potential range. A comparison of experimental and calculated passive-crevice lengths for Type 304 stainless steel and Alloy CF-8 showed good correlation.

6.1.4 Other Concentration Cells

In addition to the concentration cells discussed in Secs. 6.1.1 through 6.1.3, there are at least three additional types: hydrogen-ion, neutral-salt, and inhibitor cells. For example, high chloride-ion concentrations or low inhibitor concentrations generally are associated with anodic rather than cathodic regions on a metal surface. Furthermore, acidification of the solution within the crevice can greatly contribute to acceleration of autocatalytic crevice corrosion, especially in near-neutral solutions. The lowering of pH in crevices is probably more important than oxygen concentration gradients.

6.1.5 Unified Crevice Corrosion Mechanism

Based on the type of information developed in the preceding sections and discussed by France [118], Fontana and Greene [122] have proposed a basic mechanism of crevice corrosion:

> Initially, the anodic dissolution (e.g., $M \rightarrow M^+ + e^-$) and cathodic reduction (e.g., $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$) processes occur uniformly over the entire metal surface, including the crevice interior. The oxygen in the shielded crevice area is consumed after some incubation period, but the decrease in the cathodic reaction rate is negligible because of the small area involved. Consequently, the corrosion of the metal inside and outside the crevice continues at the same rate. With the cessation of the cathodic hydroxide-producing reaction, however, the migration of mobile negative ions (e.g., chlorides) into the crevice area is required to maintain charge balance. These processes are shown schematically in Fig. [11]. The resulting metal chlorides hydrolyze in water to insoluble metal hydroxides and free acid. Both the chloride anions and low pH accelerate crevice corrosion in a manner similar to autocatalytic pitting, while the reduction reaction cathodically protects the exterior surfaces. Also, for active-passive metals that depend on protective oxide films for their corrosion resistance, the breakdown of passivity and active corrosion in crevices are favored by the increased concentration of chlorides and hydrogen ions. This mechanism represents a rather inclusive and unifying description of crevice corrosion. It takes into account

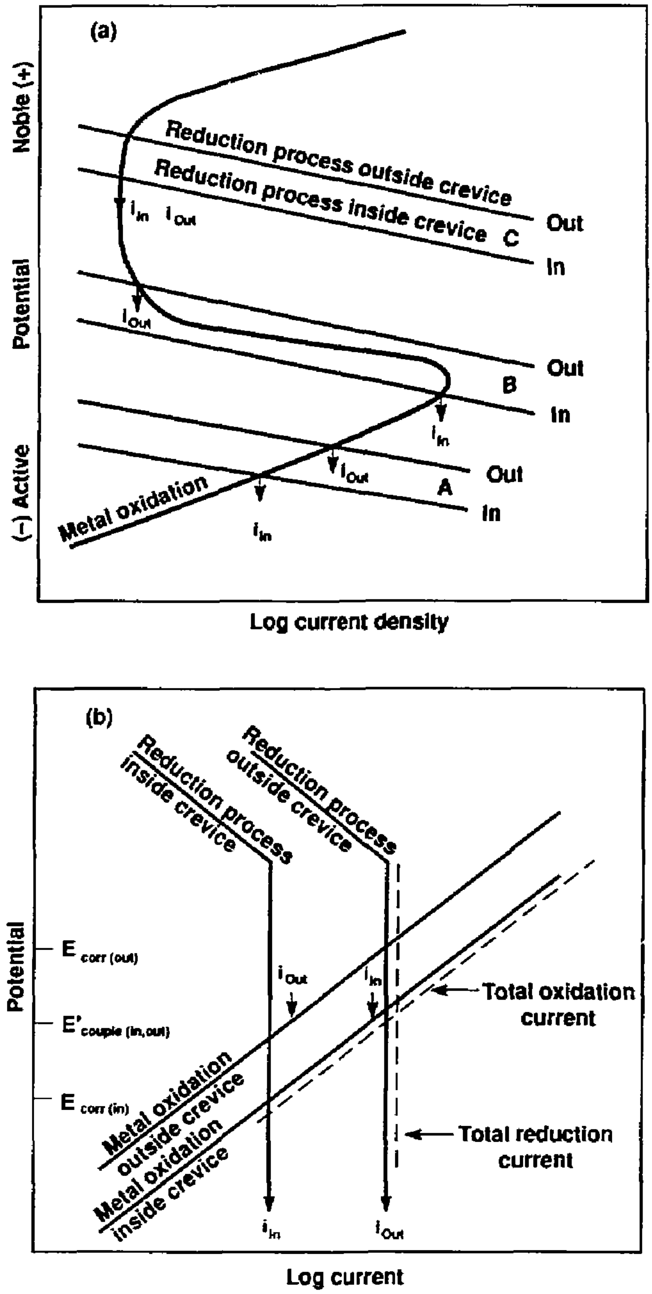

Figure 10. Schematic anodic and cathodic polarization curves for crevice corrosion analysis [118]. (a) Active-passive metal dissolution. (b) Crevice corrosion couples at active potentials.

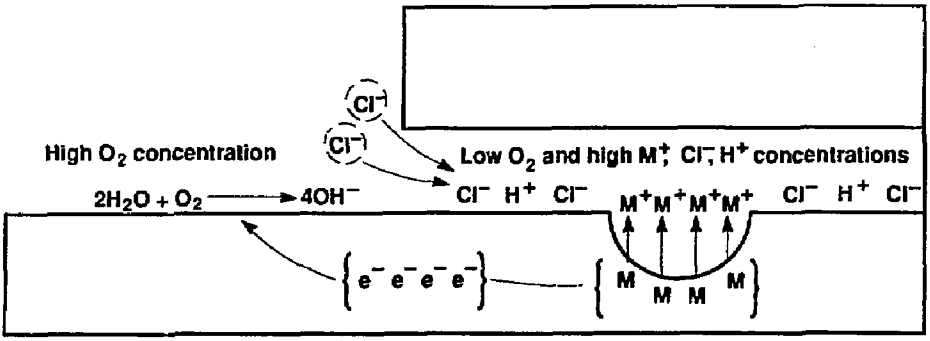

Figure 11. Fontana-Greene mechanism of crevice corrosion [122].

metal-ion concentration, oxygen depletion, hydrolysis and acidification, aggressive anion migration, and both active and active-passive dissolution behavior.

6.2 Effect of Crevice Corrosion on Other Forms of Localized Attack

Crevice corrosion can promote other forms of localized attack [118]. For example, pitting, stress corrosion cracking (SCC), exfoliation, corrosion fatigue, and intergranular corrosion can be accelerated in crevices. These types of corrosion are favored by the concentration gradients existing in crevices.

6.3 Prevention of Crevice Corrosion

It is possible to eliminate the threat of crevice corrosion and related problems by proper engineering design, which includes crevice-free fabrication, use of sacrificial anodes, and cathodic protection [118]. Unfortunately, the use of inhibitors for controlling crevice corrosion presents problems because the relative inaccessibility of the crevice site makes replenishment of depleted inhibitors difficult or impossible [118].

6.4 Tentative Ranking of Candidate Materials Based on Susceptibility to Crevice Corrosion

The selection of materials for service where crevice corrosion is a potential problem involves a comparison of their performance under conditions with crevices. However, with the possible exception of data from seawater tests, the lack of standard tests has contributed to some erratic and nonreproducible results that thwart attempts to establish meaningful rankings of materials by a comparison of data from several sources. A ranking by Tuthill and Schillmoller [123] of metals and alloys in terms of resistance to crevice corrosion in quiescent seawater is given in Table 3.

Table 3. Relative resistance of metals and alloys to crevice corrosion in quiescent seawater.

Metal or alloy	Resistance
Hastelloy C	Inert—no attack
Titanium	Inert—no attack
Cu-30Ni-0.5Fe (CDA 715)	Good—very little attack
Aluminum bronzes (CDA 613)	Good—very little attack
Alloy 825	Less—significant attack
Copper (CDA 102)	Less—significant attack
Type 316 stainless steel	Pit initiation at crevice
Type 304 stainless steel	Pit initiation at crevice

7. Tentative Ranking of the Copper-Based Alloys

Very few quantitative data were found that could be used as a basis for ranking the copper-based alloys. However, Osborn and Sudrabin have published an article on the application of these alloys in marine structures and equipment [104]. In their article, they state that copper (CDA 102) and cupronickel alloys (CDA 715) are resistant to pitting in quiescent seawater (<2 ft/s). In contrast, they state that aluminum bronze is moderately resistant to pitting. The implication is that aluminum bronze (CDA 613) has less resistance to pitting than either copper or cupronickel alloys.

Dealloying can give rise to pitting, as discussed in Sec. 5.5. It is important to note that aluminum bronze (CDA 613) also has less resistance to dealloying than does cupronickel (CDA 715). Obviously, dealloying is not a problem with pure copper (CDA 102).

In terms of susceptibility to crevice corrosion, the cupronickel alloy (CDA 715) and aluminum bronze (CDA 613) appear to be similar. Copper (CDA 102) appears to be most susceptible to this form of localized attack. Finally, biological fouling can induce localized attack of materials. Osborn and Sudrabin point out that copper (CDA 102) has the best resistance to fouling of all copper-based alloys. In contrast, cupronickel (CDA 715) and aluminum bronze (CDA 613) have only fair resistance to biofouling.

8. Summary

From these findings, one is led to believe that the following rankings might be valid for the resistance of the copper-based alloys to localized corrosion.

Pitting Corrosion:
CDA 102 = CDA 715 (best) > CDA 613 (worst)

Local Dealloying:
CDA 102 (best) > CDA 715 > CDA 613 (worst)

Crevice Corrosion:
CDA 715 = CDA 613 (best) > CDA 102 (worst)

Biofouling:
CDA 102 (best) > CDA 715 = CDA 613 (worst)

The susceptibility of CDA 102 to crevice corrosion diminishes its attractiveness as a choice, even though it performs well in the categories of pitting corrosion, local dealloying, and biofouling. The cupronickel alloy, CDA 715, probably has the best overall resistance to such localized attack.

We have not discussed the effects of gamma irradiation on the *localized* corrosion of copper and did not find any data on this topic. However, as discussed in references cited in Vol. 3, radiolysis can push the corrosion potential of both austenitic alloys and copper to more anodic levels, closer to the pitting potential. This could increase the susceptibility of the copper-based alloys to localized attack. Experimental work is needed in this area to increase our understanding of the effects of gamma radiation.

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10. References

1. "Disposal of High-Level Radioactive Wastes in Geologic Repositories, Technical Criteria," 10 CFR Part 60, Nuclear Regulatory Agency, Federal Register, Rules and Regulations, Vol. 48, No. 120, Tuesday, June 21, 1983, pp. 28194–28229. HQ2.870302.3019, HQ2.870302.3020, HQ2.870301.4065, HQ2.870301.4093
2. "Environmental Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes," 40 CFR Part 191, Environmental Protection Agency, Federal Register, Rules and Regulations, Vol. 50, No. 192, Thursday, September 19, 1985, pp. 38066–38089. HQ2.870301.5394, HQ2.870228.0739
3. R. C. Scarberry, D. L. Graver, C. D. Stephens, "Alloying for Corrosion Control: Properties and Benefits of Alloy Materials," *Materials Protection*, June 1967, pp. 54–57. NNA.890920.0233
4. G. J. Licina, "A Review of Microbial-Induced Corrosion in Nuclear Power Plant Systems," *Corrosion 88, Cervantes Convention Center, St. Louis, Missouri, March 21–25, 1988*, Paper No. 268. NNA.890920.0234
5. R. D. McCright, W. G. Halsey, R. A. Van Konynenburg, *Progress Report on the Results of Testing Advanced Conceptual Design Metal Barrier Materials Under Relevant Environmental Conditions for a Tuff Repository*, University of California, Lawrence Livermore National Laboratory, Livermore, California, UCID-21044, December 1987. HQX.80201.0016, HQS.880517.2494
6. R. Steigerwald, *Metals Handbook*, 9th edition, ASM International, Metals Park, Ohio, 1987, p. 123.
7. G. E. Gdowski, D. B. Bullen, *Oxidation and Corrosion of the Candidate Materials for the Nuclear Waste Management Program*, Science & Engineering Associates, Pleasanton, California, SEA Report 154-11, September 18, 1987.
8. H. P. Godard, "Corrosion of Metals by Waters," *Materials Performance*, May 1979, pp. 21–27. NNA.890920.0235
9. H. S. Campbell, "A Review: Pitting Corrosion of Copper and Its Alloys," *Proceedings of the U. R. Evans Conference on Localized Corrosion, Williamsburg, Virginia, December 6–10, 1971*, R. W. Staehle, B. F. Brown, J. Kruger, A. Agrawal, Editors, National Association of Corrosion Engineers, Houston, Texas, 1974, pp. 625–635. NNA.891004.0333
10. W. S. Lyman, A. Cohen, "Service Experience with Copper Plumbing Tube," *Corrosion/71, Chicago, Illinois, March 1971*, National Association of Corrosion Engineers Annual Meeting, Paper No. 84, National Association of Corrosion Engineers, Houston, Texas.
11. P. T. Gilbert, "A Review of Recent Work on Corrosion Behavior of Copper Alloys in Sea Water," *Materials Performance*, February 1982, pp. 47–53. NNA.890920.0236
12. D. H. Osborn, D. A. Sudrabin, "Copper Base Alloys: The Logical Choice for Marine Structures and Equipment," *Proceedings of the 25th Conference of the National Association of Corrosion Engineers, Houston, Texas, March 10–14, 1969*, National Association of Corrosion Engineers, Houston, Texas, pp. 318–323. NNA.890920.0237
13. A. H. Tuthill, "Guidelines for the Use of Copper Alloys in Seawater," *Materials Performance*, Vol. 26, No. 9, September 1987, pp. 12–22. NNA.890920.0238
14. K. S. Rajagopalan, M. Raghavan, N. S. Rengaswamy, T. M. Balasubramanian, V. S. Muralidharan, "Corrosion Studies on Certain Copper Based Alloys in Synthetic Sea Water Containing Traces of Ammonia," *Materials Performance*, Vol. 20, No. 1, January 1981, pp. 19–27. NNA.890920.0239
15. B. C. Syrett, S. S. Wing, "Effect of Flow on Corrosion of Copper-Nickel Alloys in Aerated Sea Water and in Sulfide-Polluted Sea Water," *Corrosion*, Vol. 36, No. 2, February 1980, pp. 73–85. NNA.890919.0311
16. B. C. Syrett, "The Mechanism of Accelerated Corrosion of Copper-Nickel Alloys in Sulphide-Polluted Sea Water," *Corrosion Science*, Vol. 21, No. 3, 1981, pp. 187–209. NNA.890919.0318
17. G. Bianchi, G. Fiori, P. Longhi, F. Mazza, "Horse Shoe Corrosion of Copper Alloys in Flowing Sea Water: Mechanism, and Possibility of Cathodic Protection of Condenser Tubes in Power Stations," *Corrosion*, Vol. 34, No. 11, November 1978, pp. 396–406. NNA.890920.0240

18. P. T. Gilbert, "A Review of Recent Work on Corrosion Behavior of Copper Alloys in Sea Water," *Materials Performance*, February 1982, Vol. 21, No. 2, pp. 47–53. NNA.890920.2036
19. C. Manfredi, S. Simison, S. R. de Sanchez, "Selection of Copper Base Alloys for Use in Polluted Seawater," *Corrosion*, Vol. 43, No. 8, August 1987, pp. 458–464. NNA.890920.0241
20. B. Little, P. Wagner, J. Jacobus, "The Impact of Sulfate-Reducing Bacteria on Welded Copper-Nickel Seawater Piping Systems," *Corrosion 88, Cervantes Convention Center, St. Louis, Missouri, March 21–25, 1988*, Paper No. 81. NNA.890920.0242
21. R. W. Ross, Jr., "The Effect of Sea Water Composition on Corrosion of Cu-Ni-Fe Alloys at Elevated Temperatures," *Materials Performance*, Vol. 18, No. 7, July 1979, pp. 15–22. NNA.890920.0243
22. R. W. Ross, Jr., D. B. Anderson, "Hot Sea Water Corrosion of Copper-Base Alloys," *Materials Performance*, Vol. 14, No. 9, September 1975, pp. 27–32. NNA.890920.0244
23. F. W. Fink, "Alloys for Sea Water Conversion," *Materials Protection*, Vol. 6, No. 5, May 1967. pp. 40–43. NNA.890920.0245
24. A. Cohen, P. F. George, "Copper Alloys in the Desalting Environment—Final Report," *Materials Performance*, Vol. 13, No. 8, August 1974, pp. 26–31. NNA.890920.0246
25. A. Cohen, L. V. Rice, "Recent Experience with Copper Alloys in Desalting Plant Environments," *Proceedings of the 25th Conference of the National Association of Corrosion Engineers, Houston, Texas, March 10–14, 1969*, National Association of Corrosion Engineers, Houston, Texas, pp. 342–345. NNA.890920.0247
26. R. N. Orava, "Stress Corrosion and Corrosion Behavior of Copper-Nickel and Titanium Under Simulated Desalinization Conditions," *Proceedings of the 25th Conference of the National Association of Corrosion Engineers, Houston, Texas, March 10–14, 1969*, National Association of Corrosion Engineers, Houston, Texas, pp. 346–358. NNA.890920.0248
27. B. C. Syrett, R. L. Coit, "Causes and Prevention of Power Plant Condenser Tube Failures," *Materials Performance*, Vol. 22, No. 2, February 1983, pp. 44–50. NNA.890920.0249
28. B. C. Syrett, R. L. Coit, "Materials Degradation in Condensers and Feedwater Heaters," *Proceedings of the International Symposium on Environmental Degradation of Materials in Nuclear Power Systems—Water Reactors, Myrtle Beach, South Carolina, August 22–25, 1983*, pp. 87–112. NNA.890920.0250
29. G. E. Moller, B. C. Syrett, *Corrosion-Related Failures in Feedwater Heaters*, Electric Power Research Institute, Palo Alto, California, EPRI Report No. CS/NP-3743, October 1984. NNA.890920.0251
30. J. A. Beavers, A. K. Agrawal, W. E. Berry, B. C. Syrett, "Corrosion Related Failures in Feedwater Heaters," *Corrosion 84, New Orleans Hilton Hotel, Rivergate Exhibition Center, New Orleans, Louisiana, April 2–6, 1984*, Paper No. 169. NNA.890920.0252
31. R. S. Pathania, J. A. Chitty, "Stress Corrosion Cracking of Steam Generator Tube Materials in Sodium Hydroxide Solutions," *Corrosion*, Vol. 34, No. 11, November 1978, pp. 369–378. NNA.890920.0253
32. P. K. De, S. K. Ghosal, "A Comparative Study of Stress Corrosion Cracking of Steam Generator Tube Materials in Water at 315°C," *Corrosion*, Vol. 37, No. 6, June 1981, pp. 341–349. NNA.890920.0254
33. S. W. Shepard, "Generalized Rules for Controlling Chemical Process Equipment Corrosion," *Corrosion*, Vol. 17, No. 3, March 1961, pp. 19–20. NNA.890920.0255
34. K. R. Walston, "Stress Corrosion Cracking of Admiralty Exchanger Tubes In Reformer Service," *Corrosion*, Vol. 17, No. 10, October 1961, p. 492t. NNA.890920.0256
35. A. F. Blumer, "Crude Still Overhead System Corrosion," *Corrosion*, Vol. 5, No. 5, May 1949, pp. 135–145. NNA.890920.0257
36. J. O. Edwards, R. I. Hamilton, J. B. Gilmour, "Early Corrosion Failures in Copper Heat Exchanger Tubing," *Materials Performance*, Vol. 16, No. 9, September 1977, pp. 18–20. NNA.890920.0258
37. S. L. Pohlman, R. V. Olson, "Corrosion and Material Problems in the Copper Production Industry," *Materials Performance*, Vol. 23, No. 12, December 1984, pp. 9–13. NNA.890920.0259
38. R. Francis, "The Effect of Chlorine Additions to Cooling Water on Corrosion of Copper Alloy Condenser Tubes," *Materials Performance*, Vol. 21, No. 8, August 1982, pp. 44–49. NNA.890920.0260
39. H. S. Campbell, "Pitting Corrosion in Copper Water Pipes Caused by Films of Carbonaceous Material Produced During Manufacture," *Journal of the Institute of Metals*, Vol. 77, No. 4, 1950, pp. 345–356.

40. V. F. Lucey, "The Mechanism of Dezincification and the Effect of Arsenic. II," *British Corrosion Journal*, Vol. 1, No. 2, September 1965, pp. 53–59. NNA.891101.0015
41. C. Breckon, J. R. T. Baines, "The Significance of Apparently Minor Factors in Corrosion Problems Affecting Condenser and Cooler Tubes," *Transactions of the Institute of Marine Engineering*, Vol. 67, No. 10, 1955, pp. 363–372.
42. H. S. Campbell, "A Review: Pitting Corrosion of Copper and its Alloys," *Localized Corrosion, NACE-3*, R. Staehle, B. Brown, J. Kruger, A. Agrawal, Editors, National Association of Corrosion Engineers, Houston, Texas, 1974, p. 625. NNA.891004.0333
43. G. L. Bailey, "Copper-Nickel-Iron Alloys Resistant to Sea-Water Corrosion," *Journal of the Institute of Metals*, Vol. 79, No. 5, 1951, pp. 243–292. NNA.891004.0334
44. J. G. N. Thomas, A. K. Tiller, "Formation and Breakdown of Surface Films on Copper in Sodium Hydrogen Carbonate and Sodium Chloride Solutions," *British Corrosion Journal*, Vol. 7, November 1972, pp. 256–262. NNA.891101.0013
45. H. S. Campbell, "Corrosion, Water Composition and Water Treatment," *Journal of Water Treatment and Examination*, Vol. 20, Part 1, 1971, pp. 11–25.
46. BNFMRA [British Non-Ferrous Metals Research Association] Miscellaneous Publication 568, December 1971 (secondary reference, quoted in Ref. 9).
47. E. Mattsson, "Corrosion of Copper and Brass: Practical Experience in Relation to Basic Data," *British Corrosion Journal*, Vol. 15, No. 1, 1980, pp. 6–13. NNA.891004.0335
48. Z. Szklarska-Smialowska, *Pitting Corrosion of Metals*, Chapter 10, "Pitting of Copper, Zinc, and Other Metals and Alloys," National Association of Corrosion Engineers, Houston, Texas, 1986. NNA.891004.0336
49. H. S. Campbell, "Pitting Corrosion in Copper Water Pipes Caused by Films of Carbonaceous Material Produced During Manufacture," *Journal of the Institute of Metals*, Vol. 77, No. 4, 1950, pp. 345–356.
50. H. S. Campbell, "A Natural Inhibitor of Pitting Corrosion of Copper in Tap-Waters," *Journal of Applied Chemistry, London*, Vol. 4, December 1954, pp. 633–647.
51. H. S. Campbell, *Water Treatment and Examination*, Vol. 3, 1954, p. 100.
52. H. S. Campbell, "Pitting Corrosion of Copper Water Pipes," *2nd International Congress on Metallic Corrosion, 1966*, p. 237. NNA.891004.0337
53. M. E. D. Turner, BNFMRA Research Report A1364, 1961 (secondary reference, quoted in Ref. 9).
54. P. Devroey, C. Depommier, Visseries et Trefileries Reunies S. A., Machelen, Belgium, unpublished report, 1962 (secondary reference, quoted in Ref. 9).
55. A. Cohen, W. S. Lyman, *National Association of Corrosion Engineers Annual Meeting, 1971*, Paper No. 84.
56. M. F. Obrecht, W. E. Sartor, J. M. Kayes, *Proceedings of the 4th International Congress on Metallic Corrosion*, in press (secondary reference, quoted in Ref. 9).
57. O. von Franque, *Werkstoffe und Korrosion*, Vol. 19, No. 5, 1968, p. 377 (secondary reference, quoted in Ref. 9).
58. V. F. Lucey, BNFMRA Research Report A 1692, 1968 (secondary reference, quoted in Ref. 9).
59. B. H. Levelton, Report to National Association of Corrosion Engineers, Technical Unit Committee T-4E, March, 1975 (secondary reference, quoted in Ref. 9).
60. E. Mattsson, A. M. Fredriksson, "Pitting Corrosion in Copper Tubes, Cause of Corrosion and Counter-Measures," *British Corrosion Journal*, Vol. 3, No. 5, September 1968, pp. 246–257. NNA.891004.0338
61. P. T. Gilbert, discussed by H. S. Campbell in "Corrosion, Water Composition and Water Treatment," *Journal of Water Treatment and Examination*, Vol. 20, Part 1, 1971, pp. 11–25.
62. H. S. Campbell, "Corrosion, Water Composition and Water Treatment," *Journal of Water Treatment and Examination*, Vol. 20, Part 1, 1971, pp. 11–25.
63. G. J. Schafer, *Australasian Corrosion Engineer*, Vol. 6, 1962, p. 15 (secondary reference, quoted in Ref. 9).
64. H. J. Boorsma, C. H. J. Elzenga, H. Nijholt, KIWA, Holland, unpublished work (secondary reference, quoted in Ref. 9).
65. K. Nielsen, Dansk VVS, Copenhagen, Vol. 8, 1971, p. 367 (secondary reference, quoted in Ref. 9).

66. A. Einarsson, G. Elisson, Idnadamal, Reykjavik, 1971 (secondary reference, quoted in Ref. 9).
67. *Verwendung von Kupferrohren in der Gas- und Wasserinstallation*, DVGW, Frankfurt, Draft Standard, August 1970 (secondary reference, quoted in Ref. 9).
68. H. S. Campbell, published discussion of P. T. Gilbert, *Water Treatment and Examination*, Vol. 15, No. 3, 1966, p. 180 (secondary reference, quoted in Ref. 9).
69. H. S. Campbell, *2nd International Congress on Metallic Corrosion*, 1966, p. 237 (secondary reference, quoted in Ref. 9).
70. G. Frommeyer, *Werkstoffe und Korrosion*, Vol. 31, No. 2, 1980, p. 114 (secondary reference, quoted in Ref. 9).
71. E. J. Cornwell, G. Wildsmith, P. T. Gilbert, ASTM STP 576, American Society for Testing and Materials, Philadelphia, Pennsylvania, p. 755 (secondary reference, quoted in Ref. 9).
72. P. Devroey, C. Depommier, Visseries et Trefileries Reunies S. A., Machelen, Belgium, unpublished work, 1965 (secondary reference, quoted in Ref. 9).
73. D. Gerth, S. B. Z., Stuttgart, Vol. 70, 1965, p. 1350 (secondary reference, quoted in Ref. 9).
74. M. Pourbaix, Reports Techniques, CEBELCOR, Vol. 100, 1965, p. 126 (secondary reference, quoted in Ref. 9).
75. R. May, "Some Observations on the Mechanism of Pitting Corrosion," *Journal of the Institute of Metals*, Vol. 32, 1953, pp. 65–74. NNA.891004.0339
76. H. S. Campbell, *Water Treatment and Examination*, Vol. 3, 1954, p. 100 (secondary reference, quoted in Ref. 9).
77. V. F. Lucey, "Mechanism of Pitting Corrosion of Copper in Supply Waters," *British Corrosion Journal*, Vol. 2, September 1967, pp. 175–185. NNA.891004.0340
78. V. F. Lucey, "Developments Leading to the Present Understanding of the Mechanism of Pitting Corrosion of Copper," *British Corrosion Journal*, Vol. 7, No. 1, January 1972, pp. 36–41. NNA.891004.0341
79. E. J. Cornwell, G. Wildsmith, P. T. Gilbert, "Pitting Corrosion in Copper Tubes in Cold Water Service," *British Corrosion Journal*, Vol. 8, No. 5, September 1973, pp. 202–209. NNA.891004.0342
80. H. Kristiansen, *Werkstoffe und Korrosion*, Vol. 28, No. 11, 1977, p. 143 (secondary reference, quoted in Ref. 9).
81. M. Pourbaix, "The Electrochemical Basis for Localized Corrosion," *Localized Corrosion, NACE-3*, R. Staehle, B. Brown, J. Kruger, A. Agrawal, Editors, National Association of Corrosion Engineers, Houston, Texas, 1974, p. 12. NNA.891004.0343
82. M. Pourbaix, J. van Muylder, P. van Laer, "Sur la tension d'electrode du cuivre en presence d'eau de bruxelles: influence de la lumiere et des conditions de circulation de l'eau," CEBELCOR Rapport Technique No. 125, 1965; *Corrosion Science*, Vol. 7, 1967, pp. 795–806. NNA.891004.0344
83. J. van Muylder, M. Pourbaix, N. de Zoubov, A. Pourbaix, CEBELCOR Rapport Technique No. 126, 1965 (secondary reference, quoted in Ref. 9).
84. J. van Muylder, M. Pourbaix, P. van Laer, CEBELCOR Rapport Technique No. 127, 1965 (secondary reference, quoted in Ref. 9).
85. P. van Laer, J. van Muylder, N. de Zoubov, M. Pourbaix, CEBELCOR Rapport No. 128, 1965 (secondary reference, quoted in Ref. 9).
86. N. de Zoubov, J. van Muylder, P. van Laer, M. Pourbaix, CEBELCOR Rapport No. 133, 1965; M. F. Obrecht, M. Pourbaix, *Proceedings of the 3rd International Congress on Metallic Corrosion, 1967*, p. 228 (secondary reference, quoted in Ref. 9).
87. U. R. Evans, *Corrosion Science*, Vol. 9, 1969, p. 813 (secondary reference, quoted in Ref. 9).
88. BNFMRA Miscellaneous Publication 538, 1971 (secondary reference, quoted in Ref. 9).
89. P. T. Gilbert, Yorkshire Imperial Metals Ltd., Leeds, private communication (secondary reference, quoted in Ref. 9).
90. M. J. N. Pourbaix, "Some Applications of Potential-pH Diagrams to the Study of Localized Corrosion," *Journal of the Electrochemical Society*, Vol. 123, No. 2, February 1976, pp. 25C–36C. NNA.891004.0345
91. M. Pourbaix, "Recent Applications of Electrode Potential Measurements in the Thermodynamics and Kinetics of Corrosion of Metals,"*Corrosion*, Vol. 25, No. 6, June 1969, pp. 267–281. NNA.891004.0346

92. M. Pourbaix, "Theoretical and Experimental Considerations in Corrosion Testing," *Corrosion Science*, 1972, Vol. 12, No. 2, 1972, pp. 161–190. NNA.891004.0347
93. J. C. Angus, C. T. Angus, "Computation of Pourbaix Diagrams Using Virtual Species: Implementation on Personal Computers," *Proceedings of an International Symposium Honoring Professor Marcel Pourbaix on His Eightieth Birthday*, The Electrochemical Society, Inc., Pennington, New Jersey, Proceedings Volume 84-9, 1984, pp. 109–134. NNA.890920.0294
94. R. W. Topham, G. Tyler Miller, Jr., "Oxidation of Copper Single Crystals in Aqueous Solutions of Inorganic Salts, II. Topography of Oxide Formed in $Cu(ClO_4)_2$ and $Cu(CHO_2)_2$ Solutions," *Journal of the Electrochemical Society*, Vol. 113, No. 5, May 1966, pp. 421–424. NNA.890920.0296
95. W. W. Porterfield, G. T. Miller, Jr., "Oxidation of Copper Single Crystals in Aqueous Solutions of Inorganic Salts, III. Kinetics of Oxidation in $Cu(OAC)_2$ Solution," *Journal of the Electrochemical Society*, Vol. 113, No. 6, June 1966, pp. 528–531. NNA.890920.0297
96. BNFMRA Miscellaneous Publication 538, 1971 (secondary reference, quoted in Ref. 9).
97. P. T. Gilbert (secondary reference, quoted in Ref. 9).
98. M. Pourbaix, Reports Techniques, CEBELCOR, Vol. 100, 1965, p. 126 (secondary reference, quoted in Ref. 9).
99. J. G. N. Thomas, A. K. Tiller, "Formation and Breakdown of Surface Films on Copper in $NaHCO_3$ and NaCl Solutions, Part 1, Effects of Anion Concentrations," *British Corrosion Journal*, Vol. 7, No. 6, November 1972, pp. 256–262.
100. E. D. Mor, A. M. Beccaria, "Effect of the Addition of Bromides and Iodides on the Corrosion of Copper in Sea Water," *British Corrosion Journal*, Vol. 12, No. 4, 1977, p. 243-246 (secondary reference, quoted in Ref. 48). NNA.891004.0356
101. J. G. N. Thomas, A. K. Tiller, "Formation and Breakdown of Surface Films on Copper in Sodium Hydrogen Carbonate and Sodium Chloride Solutions, II. Effects of Temperature and pH," *British Corrosion Journal*, Vol. 7, No. 6, November 1972, pp. 263–267. NNA.891101.0014
102. T. Fujii, T. Kodama, H. Baba, "The Effect of Water Quality on Pitting Corrosion of Copper Tube in Hot Soft Water," *Corrosion Science*, Vol. 24, No. 10, 1984, pp. 901–912. NNA.891004.0348
103. T. Fujii, T. Kodama, H. Baba, "Application of Electrochemical Techniques to the Study of Pitting Corrosion of Copper Tube in Fresh Water," *Electrochemical Methods in Corrosion Research*, M. Duprat, Ed., Materials Science Forum, Vol. 8, 1986, pp. 125–132. NNA.891004.0349
104. G. Joseph, R. Perret, Y. Spacek, "Pitting Corrosion in Copper Tubings," *Proceedings of the Fourth International Congress on Metallic Corrosion, Houston, Texas, 1969*, N. E. Hamner, Ed., National Association of Corrosion Engineers, 1972, pp. 817–822. NNA.891004.0350
105. G. L. Bailey, "Copper-Nickel-Iron Alloys Resistant to Sea-Water Corrosion," *Journal of the Institute of Metals*, Vol. 79, 1951, p. 243. NNA.891004.0334
106. D. H. Osborn, D. A. Sudrabin, "Copper Base Alloys: The Logical Choice for Marine Structures and Equipment," *Proceedings of the 25th Conference of the National Association of Corrosion Engineers, Houston, Texas, March 10–14, 1969*, National Association of Corrosion Engineers, Houston, Texas. NNA.890920.0237
107. R. Francis, "The Effect of Chlorine Additions to Cooling Water on Corrosion of Copper Alloy Condenser Tubes," *Materials Performance*, Vol. 21, No. 8, August 1982, pp. 44–49. NNA.890920.0260
108. R. Francis, "Effect of Pollutants on Corrosion of Copper Alloys in Sea Water, Part 1: Ammonia and Chlorine," *British Corrosion Journal*, 1985, Vol. 20, No. 4, pp. 167–173. NNA.891004.0351
109. R. Francis, "Effect of Pollutants on Corrosion of Copper Alloys in Sea Water, Part 2: Sulphide and Chlorine," *British Corrosion Journal*, 1985, Vol. 20, No. 4, pp. 175–182. NNA.891004.0352
110. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, New York, 1966. NNA.891005.0098
111. P.A. Candela, L.L.Y. Chang, "Solid Solution, Order Disorder, and the Thermodynamics of Alloy Corrosion," *Proceedings of an International Symposium Honoring Professor Marcel Pourbaix on His Eightieth Birthday*, Equilibrium Diagrams and Localized Corrosion, R. P. Frankenthal and J. Kruger, Editors, The Electrochemical Society, Inc., Pennington, New Jersey, Proceedings Volume 84-9, 1984, pp. 125–134. NNA.891005.0373

112. G. E. McGuire, A. L. Bacarella, J. C. Griess, R. E. Clausing, L. D. Hulett, "Analysis of Protective Oxide Films on Copper-Nickel Alloys by Auger Spectroscopy," *Journal of the Electrochemical Society*, Vol. 125, No. 11, 1978, pp. 1801–1804. NNA.890920.0288
113. R. D. K. Misra, G. T. Burstein, "The Repassivation of Nickel-Copper Alloys in Sulphuric Acid," *Corrosion Science*, Vol. 24, No. 4, 1984, pp. 305–323. NNA.890920.0298
114. M. J. Pryor, J. C. Fister, "The Mechanism of Dealloying of Copper Solid Solutions and Intermetallic Phases," *Journal of the Electrochemical Society*, Vol. 131, No. 6, June 1984, pp. 1230–1235. NNA.890920.0303
115. T. J. Lennox, M. H. Peterson, "De-Alloying of Copper Alloys and Response to Cathodic Protection in Quiescent Sea Water," *Materials Protection and Performance*, Vol. 10, No. 7, July 1971, pp. 31–37. NNA.890920.0304
116. R. J. Ferrara, T. E. Caton, "Review of Dealloying of Cast Aluminum Bronze and Nickel-Aluminum Bronze Alloys in Sea Water Service," *Materials Performance*, Vol. 21, No. 2, February 1982, pp. 30–34. NNA.890920.0305
117. L. W. Gleekman, R. K. Swandby, "Massive De-Aluminization of Aluminum Bronze by Chloride Attack," *Corrosion*, Vol. 2 , March 1961, pp. 116–120. NNA.890920.0306
118. W. D. France, Jr., "Crevice Corrosion of Metals," *Localized Corrosion—Cause of Metal Failure*, American Society for Testing and Materials, Philadelphia, Pennsylvania, ASTM STP 516, 1972, pp. 164–200. NNA.891004.0353
119. I. L. Rosenfeld, I. K. Marshakov, "Mechanism of Crevice Corrosion," *2nd International Congress on Metallic Corrosion, New York, New York, March 11–15, 1963*, National Association of Corrosion Engineers, Houston, Texas, 1966, pp. 244–255. NNA.891004.0354
120. D. A. Vermilyea, C. S. Tedmon, Jr., "A Simple Crevice Corrosion Theory," *Journal of the Electrochemical Society*, Vol. 117, No. 4, 1970, pp. 437–440. NNA.891004.0355
121. W. D. France, Jr., N. D. Greene, Jr., "Passivation of Crevices During Anodic Protection," *Corrosion*, SBIIA, Vol. 24, No. 8, 1968, p. 247 (secondary reference, quoted in Ref. 118).
122. M. G. Fontana, N. D. Greene, *Corrosion Engineering*, McGraw-Hill Book Company, New York, 1967. NNA.891018.0176
123. A. H. Tuthill, C. M. Schillmoller, *Transactions Marine Technology Society*, MTSTA, Vol. 3, 1965.