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

**Volume 2
Oxidation and Corrosion**

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List of Volumes of the Survey

This is Volume 2 of the report *Survey of Degradation Modes of Candidate Materials for High-Level Radioactive-Waste Disposal Containers*. The titles of all of the volumes are as follows:

Overview

Volume 1: Phase Stability

Volume 2: Oxidation and Corrosion

Volume 3: Localized Corrosion and Stress Corrosion Cracking of Austenitic Alloys

Volume 4: Stress Corrosion Cracking of Copper-Based Alloys

Volume 5: Localized Corrosion of Copper-Based Alloys

Volume 6: Effects of Hydrogen in Austenitic and Copper-Based Alloys

Volume 7: Weldability of Austenitic Alloys

Volume 8: Weldability of Copper-Based Alloys

Acronyms

ASTM	American Society for Testing and Materials
BWR	boiling-water reactor
CDA	Copper Development Association
CHLW	commercial high-level waste
DHLW	defense high-level waste
fcc	face-centered cubic
mdd	mg/dm ² /day
NNWSI	Nevada Nuclear Waste Storage Investigations Project
NWMP	Nuclear Waste Management Program
PWR	pressurized-water reactor
TS	tensile stress
WL	weight loss

Executive Summary

This volume discusses oxidation and corrosion of the six candidate materials for the metal containers to be used in disposing of high-level radioactive waste. Three of the candidate materials are iron- to nickel-based austenitic alloys: Types 304L and 316L stainless steels and Alloy 825. The other three are copper-based alloys: CDA 102 (oxygen-free copper), CDA 613 (Cu-7Al), and CDA 715 (Cu-30Ni).

Waste in the form of spent fuel assemblies from reactors as well as high-level waste in borosilicate glass will be sent to the prospective repository at Yucca Mountain, Nevada, for disposal. The disposal containers can undergo any of several forms of degradation in the repository during their lifetimes. The selection of the candidate material that is adequate for conditions in the repository will be based on three tasks: a survey of the literature, corrosion testing, and predictions from modeling. Lawrence Livermore National Laboratory has responsibility for all three. This volume surveys the literature on oxidation and corrosion of the candidate materials.

Part 1 of this volume provides a review of the technical literature with respect to oxidation and corrosion of the austenitic candidate alloys. Significant data are identified on the effects of atmospheric and aqueous corrosion in these alloys. A review of the basic degradation processes of oxidation and corrosion in the austenitic alloys is also presented. The wide variation in exposure conditions somewhat limits a direct comparison of the performance of different alloys.

Studies of atmospheric corrosion are believed to most closely model the expected repository environment of many packages during the first 200 to 250 yr following emplacement of the containers. Comparison of the atmospheric corrosion behavior of all the austenitic candidate alloys in the same environment indicates similar behavior following an initial transient period. A uniform corrosion rate of approximately $0.025 \mu\text{m/yr}$ has been observed for all the alloys, which would result in corrosion of $250 \mu\text{m}$ (2.5% of the container wall thickness) in 10,000 yr. The atmospheric corrosion data show that there is little distinction in corrosion rates among the three materials.

Studies of aqueous corrosion of the austenitic candidate alloys have clearly demonstrated the deleterious effects of chloride ions in the aqueous media on the protective passivation layer. Seawater exposures result in significant corrosion of Type 304 stainless steel. The addition of molybdenum as an alloying element, as in Type 316 stainless steel, enhances the resistance of the austenite to pitting and crevice corrosion attack. Further addition of nickel, as in Alloy 825, produces moderate improvement in the resistance to corrosion in a seawater environment. A comparison of data for a 1-yr immersion in seawater yields corrosion rates of $36.25 \mu\text{m/yr}$ for Type 304 stainless steel, $14.99 \mu\text{m/yr}$ for Type 316 stainless steel, and $1.01 \mu\text{m/yr}$ for Alloy 825. A seawater environment is significantly more aggressive than the proposed repository environment. However, the relative performance of the austenitic alloys in seawater might provide input on the relative resistance to oxidation and corrosion of the candidate materials.

Finally, Part 1 presents a brief review of archaeological metallurgy of iron-based material. The Delhi Pillar is described as an example of an iron structure that has survived for approximately 1600 yr. The environmental conditions of the region and the composition of the metal might have had a significant impact on the longevity of this structure. Damascus steel in the form of swords is also highlighted as an example of the survival of iron-based alloys. These swords, which date back to the Middle Ages, have survived with little observable degradation.

With respect to oxidation and general corrosion, the available data indicate that Alloy 825 performs best, followed by Type 316L stainless steel, and then by Type 304L stainless steel.

Part 2 reviews the studies of oxidation and of atmospheric and aqueous corrosion of the copper-based candidate materials. There are limited data on the candidate alloys, so where possible, data on corrosion of alloys whose compositions are similar to those of the candidate alloys have been cited. The copper-based alloys have been used extensively in marine environments, where their corrosion properties permit their use in seawater-cooled heat exchangers and in desalinization plants.

Oxidation of copper in dry air at temperatures less than 250°C proceeds at an extremely slow rate (less than $10^{-7} \mu\text{m/yr}$). An oxide layer grows by copper-ion transport through the oxide layer. This layer is protective in that it decreases the rate of oxidation. A cuprous oxide (Cu_2O) layer forms first and is adherent. The copper can be further oxidized to cupric oxide (CuO); this layer becomes exfoliative at thicknesses greater than $150 \text{ \AA}$. Additions of aluminum and nickel to copper slow the oxidation rate significantly because these metals are incorporated into the oxide layer and also form their own oxidation layer, which is impenetrable to ion transport.

Atmospheric corrosion of the copper alloys is an electrochemical process, with rates that are significantly faster than those of oxidation in dry air. The rates of corrosion at ambient temperatures vary from the lower values in dry rural environments ($<0.2 \mu\text{m}/\text{yr}$) to higher values in industrial and marine environments ($\geq 1.5 \mu\text{m}/\text{yr}$). Differences among rates of corrosion of alloys are usually within a factor of 2 for a given environment. The cupronickel and aluminum bronze alloys typically perform better than pure copper. Localized corrosion is not usually a problem during atmospheric exposure.

Aqueous environments are by far the most corrosive environments of all those reviewed. The performance of the cupronickel and aluminum bronze alloys was superior again to that of pure copper. Rates of corrosion were generally from 2 to $3 \mu\text{m}/\text{yr}$ in seawater. There was some pitting of all the alloys in seawater, with unalloyed copper being attacked the most. It is interesting that tests with seawater indicated that the rate of corrosion decreases at higher temperatures; this was thought to be due to the decreased solubility of oxygen and the increased rate of salt deposition at higher temperatures.

With respect to oxidation and general corrosion, the available data indicate that CDA 715 and CDA 613 have nearly the same performance and are more resistant than CDA 102.

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

Volume 2: Oxidation and Corrosion

Abstract

Three copper-based alloys and three iron- to nickel-based austenitic alloys are being considered as possible materials for fabrication of containers for disposal of high-level radioactive waste. This waste will include spent fuel assemblies from reactors as well as high-level waste in borosilicate glass and will be sent to the prospective site at Yucca Mountain, Nevada, for disposal. The containers must maintain substantially complete containment for at least 300 yr and perhaps as long as 1000 yr. During the first 50 yr after emplacement, they must be retrievable from the disposal site. Shortly after the containers are emplaced in the repository, they will be exposed to high temperatures and high gamma radiation fields from the decay of the high-level waste.

This volume surveys the available data on oxidation and corrosion of the iron- to nickel-based austenitic materials (Types 304L and 316L stainless steels and Alloy 825) and the copper-based alloy materials [CDA 102 (oxygen-free copper), CDA 613 (Cu-7Al), and CDA 715 (Cu-30Ni)], which are the present candidates for fabrication of the containers. Studies that provided a large amount of data are highlighted, and those areas in which little data exists are identified. Examples of successful applications of these materials are given.

On the basis of resistance to oxidation and general corrosion, the austenitic materials are ranked as follows: Alloy 825 (best), Type 316L stainless steel, and then Type 304L stainless steel (worst). For the copper-based materials, the ranking is as follows: CDA 715 and CDA 613 (both best), and CDA 102 (worst).

1. Introduction

The Nuclear Waste Management Program (NWMP) at Lawrence Livermore National Laboratory is responsible for developing the engineered barrier design to meet the Nuclear Regulatory Commission's licensing requirements for the containment of high-level nuclear waste in a potential repository in tuff. The waste will include spent fuel from civilian nuclear power plants [pressurized-water reactor (PWR) and boiling-water reactor (BWR) fuel assemblies and consolidated fuel pins]; commercial high-level waste (CHLW) in the form of borosilicate glass containing commercial spent-fuel reprocessing wastes; and defense high-level waste (DHLW) contained in borosilicate glass. The engineered containment package is being designed for emplacement in the Topopah Spring Member of the Paintbrush Tuff

at a site at Yucca Mountain, Nevada, as part of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. The reference horizon is located 350 m below the ground surface and 200 m above the static water table. The presence of oxygen gas in contact with the vadose water makes the repository conditions slightly oxidizing.

The Metal Barrier Selection and Testing Task of the NNWSI Project is responsible for the selection of the materials to be employed in the waste-package container. Six candidate materials are currently under consideration: three iron- to nickel-based austenitic materials and three copper-based materials. The austenitic materials are Types 304L and 316L stainless steels and Alloy 825. The copper-based alloy materials are CDA 102 (oxygen-free copper), CDA 613

(Cu-7Al), and CDA 715 (Cu-30Ni). The selection of the final metal barrier material is dependent on the stability of these materials in the repository environment.

The design criteria for the metal barrier require that the waste container maintain chemical and mechanical integrity for 50 yr after emplacement to permit retrieval of the nuclear waste during the preclosure phase of repository operation. These candidate materials must maintain substantially complete containment for at least 300 yr and perhaps as long as 1000 yr. This requirement implies limited failure of a few containers during this period. During these containment periods, the metal barrier will be exposed to a changing environment. A few years after emplacement, the surface of the container will reach a maximum temperature of about 250°C, which will decay to about 150°C within about 100 yr after emplacement. The early time period will also include the highest gamma radiation field from the decay of the high-level waste. The phase stability of the container material over this time period will have an impact on the mechanical and corrosion behavior of the metal barrier. Changes in the microstructure can result in considerable reduction in the fracture strength of the material. Precipitation of compounds at

grain boundaries can modify the local alloy composition, resulting in conditions more favorable to localized corrosion and certain forms of stress corrosion cracking.

This volume is one of eight that make up the survey of degradation modes [1]. The purpose of the survey is to characterize the candidate materials. The other volumes in the survey address phase stability, stress corrosion cracking, localized corrosion, effects of hydrogen, and effects of welding on container integrity.

This volume is divided into two parts. The first part deals with corrosion in the austenitic candidate materials. The second part deals with corrosion in the copper-based candidate materials. Each part summarizes the review of the literature, highlighting areas in which significant data and results exist. Each part also identifies areas in which very little data was found. Finally, examples of successful applications of these materials are given along with a ranking of the candidate materials in each group with respect to oxidation and corrosion behavior under repository-relevant conditions.

A discussion on the methodology and extent of the literature search can be found in the Overview.*

Part 1: Iron- to Nickel-Based Austenitic Candidate Materials

2. Austenitic Candidate Alloys

The austenitic alloys (Types 304L and 316L stainless steels and Alloy 825) have been selected as candidate materials for the metal barrier in the NWMP because of their moderate strength and their corrosion resistance. The typical compositions of these alloys are presented in Table 1. The resistance of the candidate materials to oxidation and corrosion under repository-relevant conditions plays an important role in the selection of a metal barrier material for repository applications. This section reviews available experimental data on the oxidation and corrosion behavior of these materials.

To promote a better understanding of the data presented in this volume, it is necessary to define the terms oxidation and corrosion with respect to repository conditions. Corrosion is usually defined as the degradation of metallic materials by chemical reaction. For the purpose of this

volume, corrosion is defined as the degradation of metallic material in an aqueous environment. Similarly, oxidation is defined as the degradation of metallic material in a vaporous or noncondensing environment. These definitions suggest that during the first century or two following emplacement, while the surface temperatures of many of the containers will be above 96°C (the unconstrained boiling temperature of water under repository ambient pressure), the dominant mode of degradation of the metal barrier in the containers should be oxidation. After the surface

* 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).

Table 1. Elemental composition of austenitic alloys (wt%).

Element	Stainless steels				Alloy 825
	304	304L	316	316L	
C	0.08 max	0.03 max	0.08 max	0.03 max	0.05 max
Mn	2.00 max	2.00 max	2.00 max	2.00 max	1.0 max
Si	1.00 max	1.00 max	1.00 max	1.00 max	0.5 max
Cr	18.0–20.0	18.0–20.0	16.0–18.0	16.0–18.0	19.5–23.5
Ni	8.0–10.5	8.0–12.0	10.0–14.0	10.0–14.0	38.0–46.0
P	0.045	0.045 max	0.045	0.045 max	—
S	0.03	0.03 max	0.03	0.03 max	0.03 max
Cu	—	—	—	—	1.5–3.0
Ti	—	—	—	—	0.6–1.2
N	0.10	0.10	0.10	0.10	—
Mo	—	—	2.0–3.0	2.0–3.0	3.0
Fe	Bal.	Bal.	Bal.	Bal.	Bal.

of a container has cooled to less than 96°C, and if water is transported to the container surface, corrosion becomes a possible mode of degradation. These definitions and modes of degradation are employed when reviewing the data on oxidation and corrosion presented in this volume.

2.1 Mechanisms of Oxidation

To comprehend the impact of oxidation on container lifetime, it is necessary to have a basic understanding of the oxidation of metals. An excellent review of oxidation of metals and alloys is presented by Morris [3]. A brief summary of that discussion is presented here to provide the essential information necessary to understand the data presented in this volume.

The rate of growth of an oxide film on the surface of a metal has a significant impact on the long-term resistance of the metal to oxidation and corrosion. This oxidation rate, which is usually limited by a diffusion step, is described by a rate law, which can take a variety of forms. A major goal of gas-metal reaction studies is the determination of an empirical rate equation and, if possible, theoretical rate equations based on the physics of the process, to delineate the kinetics of the reaction.

The simplest rate law is a linear equation, which describes the case in which the thickness of the oxide film has no effect on the rate of oxygen pickup and is directly proportional to time. If an

oxide is nonprotective (providing no barrier between the gas phase and the metal surface), the linear rate law is expected to hold. Porous or cracked oxides form on a number of metals that have been found to oxidize at a linear rate. A linear oxidation rate has also been noted for some metals that form compact, pore-free scales. These metals usually form oxides with high vacancy concentrations, permitting rapid diffusion of the base metal atoms to the surface. The rate-limiting step in this oxidation process when the oxidizing potential of the gas is low is usually controlled by surface reaction kinetics.

A parabolic oxidation rate has been observed for numerous metal systems and is based on rate control by either cation or anion diffusion across a barrier film. The oxidation rate is inversely proportional to film thickness. Hence, the growth rate of an oxide decreases with time. The rate of oxidation is controlled by the diffusion of reactants through the concentration gradient that exists across the oxide film. An expression can be derived for the rate of oxidation in terms of the specific conductivity of the oxide, the transport numbers of ions and electrons, and the decrease in free energy of the oxidation reaction. Experimental verification of expressions of this type has been obtained for a number of metal systems.

Kinetic data for thin-film formation, such as that found in most stainless steel systems, have been found to obey cubic and logarithmic rate laws. It has been suggested that thin films ($<10^{-4}$ cm) in such systems form by ion migration

under the influence of a strong electric field across the oxide. In contrast, it is thought that thick films in other systems form by thermally activated diffusion in an electrically neutral oxide.

The oxidation rates of alloys rarely follow a given rate law over a broad range of conditions, particularly at the range of moderately low temperatures expected to occur on the container surface. Variations in controlling mechanisms change the applicable rate equation, requiring that a combination of rate equations be employed to describe the reaction kinetics of the system. Hence, it is usually not possible to predict the

effects of variation of the alloy composition and/or the environment on oxidation behavior by utilizing a uniform theory. Recent advances in computer modeling coupled with increased understanding of the controlling mechanisms of oxidation might allow for more accurate prediction of oxidation kinetics for complex systems in a variety of environments.

A general classification of oxide formation, which was developed by Moreau and Benard [4], is presented in Fig. 1. This figure depicts the general classifications of scale morphologies that might occur on an alloy A-B, on the basis of

Figure 1. Oxidation modes of alloy systems [4].

experimental observations. The morphologies are divided into two classes. Class I refers to the case of selective oxidation (preferential oxidation of a single element) and is divided into two subgroups: I_A and I_B . Subgroup A delineates the selective oxidation of the minor constituent, and subgroup B represents oxidation of the major constituent. There are two possibilities for each subgroup. The oxide of the minor element, which is more reactive, might be nucleated and precipitate within the matrix of the major element; this process of formation is called internal oxidation (I_A^1). Another possibility is the formation of an oxide film of the minor element (I_A^2).

Selective oxidation of the major element also results in two possibilities, as indicated in Fig. 1. A thick oxide layer, which contains entrapped masses of the addition element, might be formed on the alloy surface (I_B), or the more noble element might concentrate at the metal-oxide interface and diffuse back into the metal phase (I_B^1).

Class II deals with the simultaneous oxidation of both constituents. Two subgroups are possible for the various modes of oxidation in Class II. Class II_A deals with insoluble oxides, where either the minor or the major constituent has the greater affinity for oxygen. When the minor element has a greater affinity for oxygen, the oxide might nucleate on the surface or precipitate as internal oxide. Since the oxide of the major element can also form, it will entrap these nuclei or precipitate as the metal oxide interface recedes. The final result is a dispersion of one oxide in the other and internal precipitates of the former in the metal phase (II_A^1). If the major element has a greater affinity for oxygen, internal oxidation does not occur as above; hence, the reduction product consists of a dispersion of oxide particles in the oxide of the major element (II_A^2).

The second subgroup of Class II addresses mixed oxides, where the two alloying elements are associated. These oxides occur most frequently at high temperatures and high oxygen potentials. The simpler case to describe is the formation of a solid solution of the oxide of one element in the oxide of the other (II_B). The other case is the formation of oxides that approach stoichiometric composition (II_B^1). This reaction often gives rise to a spinel oxide, AB_2O_4 .

The classifications presented above are actually quite general and can be used to help understand the complex problem of alloy oxidation. However, it should be noted that variation from these simple cases can occur as a result of mechanical stresses, coalescence of

oxides, and other factors that are characteristic of a particular system. Hence, care should be employed when attempting to classify a complex oxide system using the classifications in Fig. 1.

This brief introduction to the basic mechanisms of oxidation should enable the reader to better understand the potential modes of degradation for metallic materials in a vaporous or noncondensing environment.

2.2 Mechanisms of Aqueous Corrosion

As with the mechanisms of oxidation outlined in Sec. 2.1, it is worthwhile to consider the impact of aqueous corrosion as a mode of degradation on container lifetime. This requires a basic understanding of the corrosion of metals. An excellent review of corrosion of stainless steels is presented by Wallen and Olsson [5]. A brief summary of this discussion is presented here to provide the essential information necessary to better understand the data presented in this volume.

The excellent corrosion resistance of the austenitic stainless steels is a result of their capacity to become passivated. Passivity implies that, under certain circumstances, a metal or alloy will lose all chemical reactivity and will behave as an inert metal. The exact mechanisms by which passivity is achieved are still the subject of debate in the scientific community. However, the most widely accepted theory proposes the existence of an invisible oxide film. According to this theory, the metal in the passive state is covered by a very thin oxide film (10–50 Å) that is formed by reaction of the metal with the ambient environment. This film acts as a barrier between the metal and the environment, significantly reducing the rate of dissolution.

When an aqueous solution containing metal ions is in contact with a bare metal surface, both oxidation of metal atoms into metal ions and reduction of metal ions to metal atoms occur at the surface of the metal. The rate of reaction is determined by the exchange current density, i_{0M} . The reactions occur at the corrosion potential E_M^0 . Passing a current through the interface changes the potential and polarizes the electrode, which makes the oxidation and reduction subcurrents unequal. The relationship between potential, E , and current density, i , is known as the polarization curve of the metal.

Figure 2 represents a schematic anodic polarization curve for a metal that can be passivated.

Figure 2. Schematic of an anodic polarization curve representing the relationship between corrosion rate and electrode potential for a metal capable of being passivated [5].

The anodic current density is proportional to the corrosion rate of the metal. At low potentials, the metal will corrode. As the potential is increased, the rate of corrosion will rise very rapidly. This is known as the active stage of the metal. As the potential is raised further, the current will drop suddenly to a very low value, i_p , and will remain constant over an extremely wide potential range, called the passive range. Passivation of a metal requires that the passivation potential be attained (i.e., that a current density greater than the critical current density, i_c , pass through the metal electrode). Increasing the potential above the transpassive potential, E_{tr} , causes the corrosion rate to rise again since the passive film begins to dissolve; this is the transpassive region.

Factors such as temperature and pH of the corrosive medium affect the critical values E_p , i_p , i_c , and E_{tr} . Figure 3 illustrates that higher temperature and lower pH will cause i_c to increase and the width of the passive range to decrease. However, the passivation potential, E_p , and the passivation current density, i_p , are only slightly affected.

There are two electrode processes that occur on the surface of a corroding metal. The corrosion of the metal is the anodic process. The cathodic

Figure 3. Effect of pH and temperature on the corrosion rate of a metal capable of being passivated [5].

process is the reduction of an oxidizing agent such as atmospheric oxygen, which is dissolved in the electrolyte. Plotting the polarization curves for both processes on the same graph yields intersections of the curves, which indicate both the corrosion potential and corrosion rate of the metal.

Figure 4 shows a number of different situations that might occur when a metal capable of being passivated is exposed to an acid environment. This figure includes the anodic polarization curve and four cathodic polarization curves, representing four different concentrations of the oxidizing agent. When the content of oxidizing agent is low (Curve 1), the point of intersection (Point A) will lie within the active region and oxidation will occur at a high rate. At a slightly higher concentration of oxidizing agent (Curve 2), there are three points of intersection, with only two of these points (B and C) being electrically stable. The metal exhibits unstable passivity and the corrosion rate can vary from quite low (Point C) to quite high (Point B). Curve 3 represents a more highly oxidizing environment. The single intersection point lies well within the passive range (Point D). There would be very little corrosion of the base metal because of the stability of the passive film. Finally, in the excessively oxidizing electrolyte (Curve 4), the metal corrodes in the transpassive state.

Figure 4. Effect of an oxidizing agent on the corrosion rate of a metal capable of being passivated [5].

After the cathodic process has reached a certain rate, adequate amounts of the oxidizing agent will no longer be able to diffuse toward the metal surface. This is the diffusion-limited current density, i_d . Note that in Fig. 4, i_d has been plotted only for Curve 3, but it exists for all cathodic curves. If the passivity of Point D is to be stable, i_d must be greater than i_c . It should also be noted that the diffusion-limited current density rises sharply if the electrolyte is agitated or has a significant flow rate.

The examples in Fig. 4 indicate that a metal is passivated spontaneously only if the electrolyte contains an oxidizing agent that is capable of raising the corrosion current of the metal up to the critical current density, i_c . However, it is possible for a metal to be passivated without an oxidizing agent in the electrolyte. This passivation can be accomplished by making the metal an anode in an electrical circuit, which oxidizes the metal anodically. This procedure is called anodic protection and usually involves utilization of a power source such as a potentiostat to maintain the potential of the metal in the passive region of the anodic

polarization curve (Point D of Fig. 4). Under this condition, the cathodic process occurs at an auxiliary electrode immersed in the electrolyte. Utilization of anodic protection of the container material in the repository environment is not feasible, since it would require the installation of a potentiostat power source for each container or for groups of containers and would require continual maintenance to keep the power sources operational.

As indicated in the previous sections, passivity of a metal surface in an environment does not guarantee passivity of the same metal in different environmental conditions. A change in the oxidizing properties of the electrolyte can result in depletion or dissolution of the passive layer on the metal in a very short time period. Variation in the pH or temperature can result in significant changes in the passivation conditions for a metal, as highlighted in Fig. 3. This variation in oxidizing conditions must be considered over the lifetime of the container in a repository environment.

Variation in composition of the metal can have a significant impact on the corrosion

Figure 5. Comparison of the corrosion rate and electrode potential for iron and chromium [5].

resistance of an alloy. Figure 5 shows schematically the anodic polarization curves for iron and chromium in an acidic electrolyte. Note that iron is passive only at very highly positive potentials and requires a high critical current density. Also note that the transpassive potential is very high. Chromium passivates much more easily than iron, as indicated in Fig. 5. This phenomenon is due to a considerably lower passivation potential, E_p , and a passivation current, i_p , that is several orders of magnitude lower. Addition of chromium as an alloying element in an iron alloy enhances passivation considerably since chromium steels behave similarly to pure chromium. However, there is a threshold chromium level required to provide passivation of chromium steels in most neutral aqueous solutions. This minimum concentration of chromium required for passivation is about 12 wt% chromium. Experimental evidence for this passivation effect is presented in Sec. 3.3. Additions of nickel to chromium steel will further facilitate passivation, as shown in Fig. 6.

Increasing the chromium content beyond 12 wt% will produce an alloy that can be passivated in even more aggressive electrolytes. Alloying with both chromium and nickel will also dramatically increase passivation, as indicated in Fig. 6. The addition of nickel reduces i_c and results in a contraction of the active range. The passivation potential E_p is shifted slightly in the electropositive direction. This indicates that

Figure 6. Comparison of the corrosion rate and electrode potential of chromium steel and chromium-nickel steel [5].

chromium-nickel steels are more easily passivated than plain chromium steels and have a lower corrosion rate in the active range.

Addition of other alloying elements (such as molybdenum) to chromium-nickel steels further reduces i_c . This produces an alloy that is very easily passivated, even in nonoxidizing acids. Figure 7 indicates the approximate magnitudes of the critical current density for three types of stainless steel exposed to 5% sulfuric acid at room temperature. The oxidizing agent in this acid is dissolved atmospheric oxygen, which at saturation yields a diffusion-limited current density i_l with a value of approximately 100 mA/cm². This means that Type 430 chromium steel cannot be passivated under these conditions. Type 304 chromium-nickel steel is on the borderline and might or might not become passivated in this environment. Type 316 chromium-nickel-molybdenum steel can be readily passivated in this environment even if the acid is not completely saturated with atmospheric oxygen. However, it should be noted that molybdenum-bearing steels have poor properties in the transpassive region and, therefore, should not be used in highly oxidizing electrolytes. Replacement of molybdenum with silicon in chromium-nickel steels will improve corrosion resistance in the transpassive range.

The alloying elements discussed previously produce favorable effects by lowering the i_c of the

Figure 7. Anodic polarization curves for Types 304, 316, and 430 steels in 5% sulfuric acid at 25°C [5].

anodic polarization curve of the steel. Addition of a small amount of copper to these steels will not appreciably affect the polarization curve of the steel, but will facilitate the cathodic process, i.e., the reduction of the oxidizing agent. Figure 8 shows that addition of copper to the steel reduces the polarization of the cathodic reaction, which results in the steel being passivated instead of corroding in the active state.

The passive films of stainless steels are very thin, usually only 10 to 50 Å thick. These films are composed of hydrous oxides and are usually enriched in chromium, silicon, and molybdenum in comparison to the matrix material. The films are usually continuous and free of pores. The structure of the films usually corresponds to that of the underlying metal, which results in the film exhibiting different properties in areas where the steel surface is disturbed. Therefore, the passivity of the film might be impaired over discrete inclusions such as intermetallic compounds or chromium carbides or at grain boundary precipitates.

Figure 8. Effect of copper addition on the cathodic polarization curve for the corrosion of a metal capable of being passivated [5].

Other defects in the passive film might exist where the metal lattice is exposed to mechanical stresses or where slip bands intersect the surface.

Stability of the passive film might be considerably reduced in some electrolytes, particularly electrolytes containing halogen ions such as chlorides. Figure 9 illustrates schematically how the addition of chloride ions to the electrolyte affects the anodic polarization curve for steel in contact with an acid. The chloride addition reduces the width of the passive range because of the widening of the active range and the increase in current at electropositive potentials. The latter phenomenon is caused by the fact that the chloride ions at a certain potential (pitting potential) are capable of penetrating and destroying the passive film, which occurs primarily in areas where the film is weaker because of the factors discussed previously.

Passivation of the surface of a metal requires that the entire surface have access to a sufficient quantity of oxidizing agent. Should any part of the surface become shielded by foreign objects or other contamination, oxidizing-agent concentration gradients might arise. The concentration of oxidizing agent might be sufficient to maintain the passive layer in the areas exposed to the electrolyte. However, the areas beneath the contamination might have concentrations of oxidizing agent that are insufficient to maintain the passive film. Localized corrosion (pitting) might result. The issues associated with pitting, crevice corrosion, and other localized corrosive attack (such as biologically enhanced corrosion) are beyond the

Figure 9. Effect of chloride ions on the corrosion rate of a stainless steel [5].

scope of the present work. These issues are addressed in other volumes [see Ref. 1].

The brief review of aqueous corrosion presented in this section was not intended to address all of the possible modes of corrosion. The mechanisms presented here are intended to better inform the reader of the complexity of aqueous corrosion with respect to stainless steels. This information should assist the reader in understanding the results of aqueous corrosion studies presented in Sec. 3.4.

3. Degradation Studies

A review of the technical literature on oxidation and corrosion of the austenitic candidate materials revealed the existence of copious quantities of experimental data [e.g., Refs. 6–28]. A majority of the data addresses the effects of extremely severe chemical environments on the austenitic alloys. These environments include boiling magnesium chloride [18]; nitric, sulfuric, and hydrochloric acids [6, 8–11, 17, 19, 21, 23, 26]; and high-temperature, high-pressure steam [28]. The relevance of these environments to repository conditions is considered limited; hence, some of the data found in these studies will not be discussed. The references are presented at the end of this volume for the interested reader, however.

The more relevant data identified in the review of the literature can be divided into two categories, viz., data on atmospheric corrosion and data on aqueous corrosion. The atmospheric corrosion data are most applicable to the initial repository conditions, when the surfaces of many of the metal barriers will be dry because of the relatively high surface temperatures of the containers. These data on oxidation and corrosion for atmospheric exposures should be readily applicable to conditions present during the first century of repository operation. The aqueous corrosion data are more relevant to long-term repository conditions, when the surfaces of the metal barriers might be exposed to static water or condensation. The aqueous corrosion data can further be

subdivided into seawater and fresh water exposures. Corrosion in both seawater and fresh water is discussed in Sec. 3.4.

The science of corrosion encompasses a number of degradation phenomena. These include uniform or general corrosion, intergranular corrosion, pitting and crevice corrosion, stress corrosion cracking, and galvanic corrosion. Each of these mechanisms of corrosion can potentially limit the life of the metal barrier material selected for use in the repository. Uniform corrosion and oxidation are addressed in this volume. Volume 3 addresses the effects of stress corrosion cracking and localized corrosion on the behavior of austenitic candidate materials, Vol. 4 addresses the effects of stress corrosion cracking on the behavior of copper-based candidate materials, and Vol. 5 addresses the effects of localized corrosion on the behavior of copper-based candidate materials.

3.1 A Brief History of the Austenitic Materials

Several factors influence the corrosion resistance of metal alloys, including metal composition, heat treatment, mechanical processing history, and impurity content. The primary reason for the corrosion resistance of austenitic alloys is the formation of a thin hydrous oxide film on the surface of the metal. The film varies in composition from alloy to alloy and with different manufacturing treatments (such as pickling, rolling, and heat treatment). This film, which is stabilized by chromium, is usually considered to be continuous, nonporous, insoluble, and self-healing for any stainless steel alloy. The self-healing aspect of this oxide film is only operative when the alloy is exposed to air or a suitable oxidizing agent.

Passivity is the corrosion-resistant behavior produced by the presence of a passive oxide film. This is not a constant state in stainless materials, but exists over a range of conditions. This range of conditions might be broad or narrow, with the possibility of passivity being destroyed by a slight change in these conditions. Under conditions that favor passivity, stainless steels have corrosion potentials approaching those of noble metals. When passivity is destroyed, the corrosion potential approximates that of ordinary iron. The passive chromium oxide surface layer is extremely tenacious and resistant to many aqueous and oxidizing environments.

The beneficial effect of the addition of chromium to iron alloys was first documented in the early 1800s. Chromium-iron alloys were reported to have increased corrosion resistance as early as 1820 in a paper published by Stodart and Faraday [29]. However, the maximum chromium content they employed was below that required for passivity. The first austenitic alloy steels were developed at the Krupp Steel Works in Germany from 1912 to 1914 and were based on the research of E. Maurer and B. Strauss [5]. Alloy 825 was developed in the 1930s by the International Nickel Corporation as a material that is resistant to hot corrosive acids.

Work on the development of austenitic alloys continued throughout the early part of the 20th century, with significant improvements in the resistance of these materials to oxidation and corrosion. Variation of the chromium content and the additions of alloying elements such as molybdenum, titanium, and copper enhanced the stability of the passive oxide layer in various aggressive environments. The effect of composition on the oxidation and corrosion behavior of the austenitic candidate materials is further described in Sec. 3.2.

3.2 Effect of Composition on Corrosion Behavior

Most of the corrosion-resistant characteristics of stainless steels are derived from the presence of chromium. An increase in the chromium content to greater than about 12 wt% dramatically reduces the corrosion of stainless steels in many types of atmospheres. This effect is clearly indicated in Figs. 10 and 11 for various atmospheric exposure environments [30]. These figures highlight the effects of increasing chromium content on the corrosion penetration of iron-chromium alloys in various environments. Figure 10 shows the average penetration as a function of chromium content for semirural and industrial environments. Figure 11 shows the average penetration as a function of chromium content for moderate marine and severe marine environments. Note that, at a chromium content of approximately 12 wt%, the average penetration drops to near zero in all environments.

Another study of the effects of chromium content on the corrosion behavior of iron-chromium alloys in atmospheric corrosion tests conducted in a marine environment was

Figure 10. Effect of increasing chromium content on the corrosion of stainless steels during atmospheric exposures in semirural and industrial environments after an 8-yr exposure [50].

completed by Faulring [31]. Figure 12 shows weight loss vs chromium content for various austenitic samples exposed for 25.07 yr at Kure Beach, North Carolina. Note that, at a chromium content of about 12 wt%, the corrosion rate approaches zero for these tests, which is similar to the results presented in the previous two figures.

The presence of nickel in high-chromium stainless steels greatly reduces the corrosion of these alloys in certain nonoxygenating environments. This is thought to be due to the stabilization of the passive oxide layer by additions of nickel. Nickel might not add significant corrosion resistance in some atmospheric environments. However, nickel imparts significant beneficial characteristics to the alloy by acting as an austenite stabilizer, as described in Vol. 1 [1].

The addition of moderate amounts of molybdenum to stainless steels greatly improves the resistance of these materials to corrosion by halogen salt solutions and suppresses pitting in seawater. Addition of molybdenum strengthens the passive film in some environments in which it is otherwise unstable, thereby reducing the incidence of pitting. However, when failure of the passive layer occurs in Type 316 stainless steel, the pits

formed are usually as deep as those observed in molybdenum-free grades such as Type 304 stainless steel. Pitting in Type 316 stainless steel might also occur under foreign deposits that prevent oxygen from reaching the passivated surface or in areas where halogen salt concentrations are sufficiently high.

Other alloying elements of interest with respect to corrosion resistance in the austenitic candidate alloys include titanium and copper. Alloy 825 contains 0.6 to 1.2 wt% titanium and 1.5 to 3.0 wt% copper. Titanium acts to limit the effects of sensitization. Sensitization results from the depletion of chromium in the passivation layer near grain boundaries because of the formation of chromium carbide precipitates during heat treatment or welding. The presence of titanium inhibits the growth of chromium carbide precipitates by limiting the carbon activity by the formation of titanium carbide precipitates, which prevents chromium depletion and the resulting possibility of intergranular corrosion attack. The addition of copper to a nickel-iron-chromium alloy improves resistance of the alloy to hot sulfuric acid solutions. Hence, the addition of a small amount (a few percent) of copper can have

Figure 11. Effect of increasing chromium content on the corrosion of stainless steels during atmospheric exposures in moderate and severe marine environments after an 8-yr exposure [50].

a substantial impact on the corrosion resistance of an austenitic alloy that must survive in an environment containing sulfur.

3.3 Atmospheric Corrosion of the Austenitic Candidate Alloys

Numerous studies of the oxidation and corrosion behavior of metallic materials in atmospheric environments at various geographic locations have been completed [30–48]. An excellent review of atmospheric corrosion of stainless steel has been completed by Johnson and Pavlik [30]. This section highlights studies of atmospheric corrosion that present data that might be relevant to repository conditions.

Copson [32–37] completed a number of atmospheric exposures of steels at various locations

around the country from the 1930s through the 1950s. Initial tests were completed on low-alloy and structural steel samples. These tests also documented weather patterns and the effects of sheltered vs bold exposure of the specimens. Copson later also studied the atmospheric corrosion of some nickel alloys, including Alloy 825 [37]. Copson spent a great deal of time and effort planning and evaluating experimental studies of atmospheric corrosion. He also completed an extensive review of the theory of corrosion of low-alloy steels in the atmosphere [32].

Wesley and Copson reported on an experimental study of the weathering behavior of insect screen materials in 1946 [36] that included exposures of Type 316 stainless steel and 18-8 corrosion-resistant steel (for the purposes of this review, the composition of the 18-8 steel is considered to be similar to that of Type 304

Figure 12. Weight loss vs chromium content for various austenitic alloys exposed for 25.07 yr to the marine environment at Kure Beach, North Carolina [31].

stainless steel). These screens were exposed to sulfurous, industrial, marine, and rural environments between 1932 and 1943. Some samples were boldly exposed while others were sheltered from cleansing rainfall. The results of these tests showed no significant corrosion in the Type 316 stainless steel screen materials and only slight pitting in the marine environment. The 18Cr-8Ni

stainless steel suffered from significant pitting in industrial and marine environments.

The effects of chromium on the atmospheric corrosion of iron-chromium alloys was studied by Franks [49]. Low-carbon steel samples containing from 0 to 17.26 wt% chromium were prepared. These samples were boldly exposed to industrial atmospheres for up to 10 yr in Long Island City,

New York, and Niagara Falls, New York. Franks noted that "as the chromium content is increased to 12 and 17%, the steels become practically immune to attack." Similar results were obtained by Binder and Brown [44] for atmospheric corrosion tests completed on low-carbon, chromium (0-18 wt%) steels. The atmospheric exposures were completed at Kure Beach, North Carolina; Niagara Falls, New York; and New York, New York; over a period of approximately 5 yr.

Investigations by Schmitt and Mullen [50] included atmospheric tests of steels containing 0.01 to 28% chromium in semirural, industrial, and marine environments. After 8 yr of exposure, it was concluded that steels containing 12 wt% or more chromium resist corrosion in industrial and semirural environments. The results of Schmitt and Mullen, summarized in Figs. 10 and 11, are similar to the results obtained by Faulring and indicate that, for chromium contents greater than about 12 wt%, there is little degradation of iron-chromium alloys under atmospheric conditions.

Other significant atmospheric studies, which were completed in various environments, have included the austenitic candidate materials. A summary of some of the data obtained in these studies is provided in Table 2. For Type 304 stainless steel, studies have been completed by Copson [51] and Truman [52] in marine and urban environments, respectively. Copson noted no measurable corrosion for Type 304 stainless steel boldly exposed to a marine environment in Bayonne, New Jersey, for 11.88 yr. Samples of Type 304 stainless steel that were exposed in a sheltered environment corroded at a rate of $0.062 \text{ mg/dm}^2/\text{day}$ (mdd). Truman exposed Type 304 stainless steel to an urban environment with exposures beginning at three different times. The initial exposures were begun in 1938 and continued through 1942. The corrosion rate measured for these exposures was 0.0427 mdd. Subsequent exposures begun in 1962 and 1964 and lasting 5 yr each had corrosion rates of 0.017 and 0.012 mdd, respectively. The decrease in corrosion rate noted by Truman for similar exposures at the same location was attributed to a reduction in the level of air pollution at the Sheffield, England, exposure site.

Copson [51] also completed atmospheric corrosion studies of Type 316 stainless steel in Bayonne, New Jersey. This work identified no corrosive degradation of Type 316 stainless steel in either bold or sheltered exposures over

11.88 yr. The results for the Type 316 stainless steel exposures by Copson indicate that, in the marine environment of Bayonne, New Jersey, Type 316 stainless steel performs better than Type 304 stainless steel. Exposures of Type 316 stainless steel to the urban environment of Sheffield, England, by Truman [52] provide a similar means of comparison between Types 304 and 316 stainless steels. Type 316 stainless steel showed significantly less corrosion than did Type 304 stainless steel for identical exposures, as highlighted in Table 2. Type 316 stainless steel had a corrosion rate approximately 4 to 5 times less than the corrosion rate for Type 304 stainless steel subjected to the same environmental conditions.

Atmospheric corrosion studies completed by Southwell et al. [53-58] in conjunction with materials development work for the Panama Canal provide another significant set of atmospheric corrosion data. The results of these exposures are summarized in Table 2. Exposure of Type 316 stainless steel to coastal and inland atmospheric environments in the Panama Canal Zone for periods up to 16 yr resulted in no measurable corrosion in either environment. These studies also included atmospheric exposure of a 17Cr-7Ni stainless steel in coastal and inland atmospheric environments. The composition of this steel, which is similar to that of Type 304 stainless steel, provides an indication of the expected behavior of Type 304 stainless steel in a similar environment. The 17Cr-7Ni steel exposed to the coastal atmospheric conditions exhibited very slight corrosion ($0.016\text{-}0.125 \text{ }\mu\text{m/yr}$), with a weight loss of 0.005 to 0.027 mdd. Figure 13 shows a plot of the variation in corrosion rate as a function of time for the 17Cr-7Ni alloy in coastal and inland atmospheric environments in the Panama Canal Zone. Note that, in a coastal (marine) environment, the corrosion rate is $0.125 \text{ }\mu\text{m}$ after an exposure of 1 yr. This corrosion rate decreases to $0.016 \text{ }\mu\text{m}$ at 8 yr and increases to $0.023 \text{ }\mu\text{m/yr}$ after 16 yr of exposure.

It should be noted that this study provides relatively long-term data that allow direct comparison between alloys similar to Types 304 and 316 stainless steels in moist atmospheric environments under identical conditions. Type 316 stainless steel exhibited no degradation in the coastal or inland exposures over the entire 16-yr period of the test. Type 304-like stainless steel, though not severely corroded, did exhibit some

Table 2. Atmospheric corrosion studies of austenitic alloys.

Candidate alloy	Type of study	Weight loss (mdd)	Corrosion rate ($\mu\text{m}/\text{yr}$)	Exposure time (yr)	Comment	Ref.
304	Marine	0.062	0.283	11.88	Sheltered exposure, Bayonne, New Jersey	51
304	Marine	0.0	0.0	11.88	Bold exposure, Bayonne, New Jersey	51
304	Urban	0.0427	0.195	5.0	1938 exposure, Sheffield, England	52
304	Urban	0.017	0.078	5.0	1962 exposure, Sheffield, England	52
304	Urban	0.012	0.055	5.0	1964 exposure, Sheffield, England	52
17-7	Marine	0.0274	0.125	1.0	Panama Canal Zone, coastal atmosphere	53
17-7	Marine	0.0034	0.016	8.0	Panama Canal Zone, coastal atmosphere	53
17-7	Marine	0.0051	0.023	16.0	Panama Canal Zone, coastal atmosphere	53
17-7	Rural	0.0	0.0	1.0	Panama Canal Zone, inland atmosphere	53
17-7	Rural	0.0034	0.016	8.0	Panama Canal Zone, inland atmosphere	53
17-7	Rural	0.0	0.0	16.0	Panama Canal Zone, inland atmosphere	53
302	Marine	0.0050	0.023	5.0	Kure Beach, North Carolina, 25 m from surf	59
302	Marine	0.0	0.0	5.0	Kure Beach, North Carolina, 250 m from surf	59
302	Industrial	0.0006	0.0025	4.92	Bridgeport, Connecticut	59
302	Rural	0.0	0.0	2.0	Saskatoon, Canada	30
302	Semirural	0.0	0.0	2.0	Ottawa, Canada	30
302	Semirural	0.0	0.0	2.0	Trail, Canada	30
302	Rural-marine	0.0	0.0	2.0	Halifax, Nova Scotia, Canada	30
302	Rural-marine	0.0	0.0	2.0	Esquimaux, Canada	30
302	Industrial	0.0	0.0	2.0	Montreal, Canada	30
302	Industrial	0.0108	0.050	2.0	Halifax, Nova Scotia, Canada	30
316	Marine	0.0	0.0	11.88	Sheltered, Bayonne, New Jersey	51
316	Marine	0.0	0.0	11.88	Bold exposure, Bayonne, New Jersey	51
316	Urban	0.002	0.009	5.0	1938 exposure, Sheffield, England	52
316	Urban	0.003	0.014	5.0	1962 exposure, Sheffield, England	52
316	Urban	0.003	0.014	5.0	1964 exposure, Sheffield, England	52
316	Urban	0.003	0.014	5.0	1965 exposure, Sheffield, England	52
316	Marine	0.0	0.0	1.0	Panama Canal Zone, coastal atmosphere	53
316	Marine	0.0	0.0	8.0	Panama Canal Zone, coastal atmosphere	53
316	Marine	0.0	0.0	16.0	Panama Canal Zone, coastal atmosphere	53
316	Rural	0.0	0.0	1.0	Panama Canal Zone, inland atmosphere	53
316	Rural	0.0	0.0	8.0	Panama Canal Zone, inland atmosphere	53
316	Rural	0.0	0.0	16.0	Panama Canal Zone, inland atmosphere	53
316	Marine	0.0072	0.033	5.0	Kure Beach, North Carolina, 25 m from surf	59
316	Marine	0.0	0.0	5.0	Kure Beach, North Carolina, 250 m from surf	59
316	Industrial	0.0017	0.008	4.92	Bridgeport, Connecticut	59
316	Rural	0.0	0.0	2.0	Saskatoon, Canada	30
316	Semirural	0.0	0.0	2.0	Ottawa, Canada	30
316	Semirural	0.0	0.0	2.0	Trail, Canada	30
316	Rural-marine	0.0	0.0	2.0	Halifax, Nova Scotia, Canada	30
316	Rural-marine	0.0	0.0	2.0	Esquimaux, Canada	30
316	Industrial	0.0	0.0	2.0	Montreal, Canada	30
316	Industrial	0.0065	0.030	2.0	Halifax, Nova Scotia, Canada	30
825	Marine	0.034	0.152	2.0	Kure Beach, North Carolina	37
825	Marine	0.007	0.025	7.0	Kure Beach, North Carolina	37
825	Urban	0.026	0.127	2.0	Newark, New Jersey	37
825	Urban	0.004	0.025	7.0	Newark, New Jersey	37
825	Marine	0.040	0.178	2.0	Point Reyes, California	37
825	Rural	0.024	0.102	2.0	State College, Pennsylvania	37
825	Rural	0.005	0.025	7.0	State College, Pennsylvania	37

Figure 13. Atmospheric corrosion rate for coastal and inland exposures of Type 304 stainless steel [53].

measurable weight loss. Type 316 stainless steel was clearly superior to the Type 304-like stainless steel under these conditions.

Another atmospheric corrosion study that permits comparisons between a "Type 304-like" stainless steel and Type 316 stainless steel in marine and industrial environments was completed by Bomberger et al. [59]. This study included atmospheric exposures of Type 316 stainless steel at two locations: Kure Beach, North Carolina (25 m and 250 m from surf) and Bridgeport, Connecticut. The exposures were completed over approximately 5 yr using numerous materials. The Type 304-like stainless steel employed in this study was Type 302 stainless steel. This material is similar to Type 304 stainless steels in chromium and nickel content. Type 302 stainless steel has slightly less manganese and silicon but higher carbon than does Type 304 stainless steel. However, since long-term concurrent exposure data for Types 304 and 316 stainless steels are somewhat rare, it is appropriate that the results for Types 302 and 316 stainless steels be presented. As indicated in Table 2, neither the Type 304 stainless steel nor the Type 316 stainless steel specimens exhibited any corrosion or weight loss when exposed for 5 yr to atmospheric conditions at a position 250 m

from the shore in Kure Beach, North Carolina. Slight corrosion was noted following exposure to an industrial environment for 4.92 yr at Bridgeport, Connecticut, for both Type 302 stainless steel (0.0025 µm/yr) and Type 316 stainless steel (0.008 µm/yr). More significant corrosion was noted when both alloys were exposed to marine conditions 25 m from the shore at Kure Beach, North Carolina (0.023 µm/yr in Type 302 and 0.033 µm/yr in Type 316). It is interesting to note that Type 302 stainless steel exhibited slightly less corrosion than did the Type 316 stainless steel in the severe marine and industrial environments.

Another significant study of atmospheric corrosion of Types 302 and 316 stainless steels in various environments was completed in Canada by Gibbons (as referenced by Johnson and Pavlik [30]). This study consisted of 2-yr atmospheric exposures of Types 302 and 316 stainless steels at seven different locations in Canada. The types of atmospheric conditions ranged from a rural environment in Saskatoon to an industrial environment in Halifax, Nova Scotia. The results of this study are summarized in Table 2 for both Types 302 and 316 stainless steels. Gibbons noted no measurable corrosion in either Type 302 stainless steel or Type 316 stainless steel exposed for

2 yr at Saskatoon, Ottawa, Trail, Halifax (rural marine), Esquimaux, or Montreal. The only measurable corrosion was noted for both Types 302 and 316 stainless steels exposed for 2 yr in the industrial atmosphere of Halifax. The corrosion rate noted for Type 302 stainless steel ($0.050 \mu\text{m}/\text{yr}$) was slightly greater than that observed for Type 316 stainless steel ($0.030 \mu\text{m}/\text{yr}$).

Atmospheric corrosion data for Alloy 825 are very limited. The most comprehensive study was completed by van Rooyen and Copson [37]. This investigation consisted of atmospheric exposures of various nickel alloys, including Alloy 825, at four sites across the United States for periods up to 7 yr. Two marine sites, Kure Beach, North Carolina, and Point Reyes, California, were selected. The other two sites included an industrial site at Newark, New Jersey, and a rural site at State College, Pennsylvania. The results of these exposures are presented in Table 2. The data on weight loss and corrosion rates from these studies are also plotted as a function of exposure time in Figs. 14 and 15. Note that there are no data available for Point Reyes, California, after 2 yr. The samples were destroyed by vandals prior to the completion of the 7-yr period.

The corrosion rate for atmospheric exposure of Alloy 825 was greatest for all sites after 2 yr.

This result was most likely due to the initial formation of the protective oxide passivation layer. The marine exposures had the greatest corrosion rate during the initial period of the experiment. The highest corrosion rate was measured at Point Reyes ($0.178 \mu\text{m}/\text{yr}$). The Kure Beach, North Carolina 2-yr corrosion rate was $0.152 \mu\text{m}/\text{yr}$. The urban environment of Newark, New Jersey, had a 2-yr corrosion rate of $0.127 \mu\text{m}/\text{yr}$. The lowest 2-yr corrosion rate was measured in the rural environment of State College, Pennsylvania, where the corrosion rate was $0.102 \mu\text{m}/\text{yr}$. After 7 yr of atmospheric exposure, the corrosion rates for all environments decreased significantly. The corrosion rate for all locations was the lowest measurable value of $0.001 \text{ in.}/\text{yr}$ ($0.025 \mu\text{m}/\text{yr}$), as shown in Fig. 15. This implies that, after an initial period of oxidation in which the passivation layer is stabilized, the corrosion rate of Alloy 825 in these atmospheric conditions appears to be independent of environment.

In all of the corrosion data presented, there was only one location where corrosion studies were completed on all three candidate alloys: Kure Beach, North Carolina. Type 302 (similar to 304) and Type 316 stainless steels were exposed at Kure Beach by Bomberger [59], and Alloy 825 was exposed at Kure Beach by van Rooyen and

Figure 14. Average weight loss for atmospheric exposure of Alloy 825 in various environments [37].

Figure 15. Average corrosion rate for atmospheric exposure of Alloy 825 in various environments [37].

Copson [37]. A comparison of the results of these two studies should provide a basis for comparison of the behavior of the candidate alloys in the same environment. Figure 16 shows a plot of the corrosion rates of the austenitic candidate alloys exposed at Kure Beach, North Carolina. Initially, Alloy 825 appears to have a significantly higher corrosion rate. However, data are not available for Types 302 and 316 stainless steels during the first few years of exposure. Therefore, it is not known whether similar, higher corrosion rates could be expected for these alloys initially. The most obvious trend that can be discerned from these data is that, after more than 5 yr, there appears to be little difference in the corrosion rates of any of the austenitic candidate alloys; all corrode at a rate of about $0.025 \mu\text{m}/\text{yr}$. Therefore, on the basis of atmospheric corrosion results, there appears to be little difference between the alloys in the same environment. Hence, differences in the behavior of the austenitic candidate alloys immersed in aqueous corrosion environments might have a greater impact on metal barrier material selection with respect to oxidation and corrosion.

3.4 Aqueous Corrosion of the Austenitic Candidate Alloys

A review of the technical literature with respect to aqueous corrosion of the austenitic candidate alloys revealed several corrosion studies [53–68] that might have direct application to materials degradation under repository-relevant conditions. These studies encompassed a wide variety of exposure conditions, ranging from seawater [53–59, 61, 64] and fresh water [53–58, 63], to geothermal water [62] and superheated steam [28, 67, 68]. An excellent review of corrosion of metals in marine environments is presented by Fink and Boyd [66]. This work includes evaluations of both the austenitic and copper-based candidate alloys of interest. A summary of some of the aqueous corrosion data that have been identified in this study is presented in Table 3.

One difficulty encountered in the interpretation of the data available in the technical literature relates to the mode of degradation in each environment. The primary mode of degradation for passivated materials in an aqueous environment

Figure 16. Comparison of average corrosion rates of the austenitic candidate alloys exposed at Kure Beach, North Carolina. Data for Types 302 and 316 stainless steels are from Bomberger [59], and data for Alloy 825 are from Van Rooyen and Copson [37].

Table 3. Aqueous corrosion studies of austenitic alloys.

Candidate alloy	Type of study	Weight loss (mdd)	Corrosion rate (μm/yr)	Exposure time (yr)	Comment	Ref.
302	Seawater	7.945	36.25	1.0	Immersion test, Panama Canal	53
302	Seawater	3.767	17.19	8.0	Immersion test, Panama Canal	53
302	Seawater	3.202	14.61	16.0	Immersion test, Panama Canal	53
302	Seawater	1.096	5.00	1.0	Mean tide test, Panama Canal	53
302	Seawater	0.616	2.81	8.0	Mean tide test, Panama Canal	53
302	Seawater	0.565	2.58	16.0	Mean tide test, Panama Canal	53
302	Lake water	0.0	0.0	1.0	Immersion test, Panama Canal	53
302	Lake water	0.0	0.0	8.0	Immersion test, Panama Canal	53
302	Lake water	0.0	0.0	16.0	Immersion test, Panama Canal	53
302	Seawater	0.45	2.03	1.32	Pitting, flowing seawater	59
302	Seawater	0.49	2.24	4.5	Pitting, flowing seawater	59
302	Seawater	0.82	3.71	1.32	Pitting, stagnant seawater	59
304	Seawater	5.91 ^a	26.96	0.34	5640-ft depth, deep sea test	61
304	Seawater	8.51 ^a	38.83	2.06	5640-ft depth, deep sea test	61
304	Seawater	5.31 ^a	24.23	2.92	5300-ft depth, deep sea test	61
304	Seawater	3.15 ^a	14.37	1.06	Ocean surface	61
304	Steam	0.760	3.47	1.13	Superheated steam at 566°C	28
304	Steam	2.123	9.69	1.13	Superheated steam at 621°C	28
304	River water	—	65.77 ^a	0.30	Colorado River water, 100 mg/l Cl, clean	63
304	River water	—	40.56 ^a	0.25	Colorado River water, 200 mg/l Cl	63
304	River water	—	533.33 ^a	0.30	Colorado River water, 300 mg/l Cl, clean	63
304	River water	—	91.25 ^a	0.33	Colorado River water, 600 mg/l Cl	63

Table 3. (Continued.)

Candidate alloy	Type of study	Weight loss (mdd)	Corrosion rate ($\mu\text{m}/\text{yr}$)	Exposure time (yr)	Comment	Ref.
304	River water	—	81.11 ^a	0.50	Colorado River water, 1000 mg/l Cl	63
304	Seawater	—	56.76 ^a	1.34	Pitting in quiescent seawater	64
304	Seawater	—	14.28 ^a	1.78	Pitting in quiescent seawater	64
316	Seawater	3.285	14.99	1.0	Immersion test, Panama Canal	53
316	Seawater	1.403	6.4	8.0	Immersion test, Panama Canal	53
316	Seawater	0.274	1.25	16.0	Immersion test, Panama Canal	53
316	Seawater	0.274	1.25	1.0	Mean tide test, Panama Canal	53
316	Seawater	0.137	0.63	8.0	Mean tide test, Panama Canal	53
316	Seawater	0.034	0.16	16.0	Mean tide test, Panama Canal	53
316	Lake water	0.0	0.0	1.0	Immersion test, Panama Canal	53
316	Lake water	0.0	0.0	8.0	Immersion test, Panama Canal	53
316	Lake water	0.0	0.0	16.0	Immersion test, Panama Canal	53
316L	Geothermal	1.11 ^a	5.06	—	Pitting at 20°C, Utah water	62
316L	Geothermal	2.22 ^a	10.13	—	Pitting at 50°C, Utah water	62
316L	Geothermal	13.89 ^a	63.37	—	Pitting at 60°C, Utah water	62
316L	Geothermal	2.50 ^a	11.41	—	Pitting at 75°C, Utah water	62
316L	Geothermal	1.94 ^a	8.85	—	Pitting at 95°C, Utah water	62
316	Seawater	0.89	4.06	1.32	Pitting, flowing seawater	59
316	Seawater	0.34	1.55	4.5	Pitting, flowing seawater	59
316	Seawater	1.34	6.11	1.32	Pitting, stagnant seawater	59
316	River water	—	0.0	0.30	Colorado River water, 100 mg/l Cl, clean	63
316	River water	—	0.0	0.25	Colorado River water, 200 mg/l Cl	63
316	River water	—	0.0	0.30	Colorado River water, 300 mg/l Cl, clean	63
316	River water	—	0.0	0.33	Colorado River water, 600 mg/l Cl	63
316	River water	—	0.0	0.50	Colorado River water, 1000 mg/l Cl	63
316	Seawater	—	18.92 ^a	1.34	Pitting in quiescent seawater	64
316	Seawater	—	57.14 ^a	1.78	Pitting in quiescent seawater	64
825	Seawater	0.634	2.94	0.34	5640-ft depth, deep sea test	61
825	Seawater	2.31 ^a	10.73	2.06	5640-ft depth, deep sea test	61
825	Seawater	0.218 ^a	1.01	1.06	Ocean surface	61
825	Steam	0.400	1.86	1.13	Superheated steam at 566°C	28
825	Steam	0.110	0.51	1.13	Superheated steam at 621°C	28

^aWeight loss or corrosion rate is attributed largely to localized corrosion.

containing chloride ions is localized corrosion in the form of pitting or crevice corrosion. These modes of degradation are not the focus of this volume but are addressed in detail in Vols. 3 and 5. However, since it is difficult to completely separate pitting and crevice corrosion in seawater environments from general corrosion, some results for pitting and crevice corrosion in seawater environments are presented here.

The most extensive aqueous corrosion study that included candidate materials or materials similar to candidate materials was completed by Southwell et al. [53–58]. This study was undertaken to identify materials suitable for application in the harsh environments of the Panama Canal.

The experiment, which included atmospheric and aqueous exposure of numerous materials, lasted 16 yr. The austenitic materials of interest that were exposed to aqueous environments are Types 302 and 316 stainless steels. The Type 302 stainless steel employed in this study, though not having exactly the same composition as Type 304 stainless steel, was composed of 18Cr-8Ni. For the purposes of this survey of degradation modes, the data from the Type 302 stainless steel exposures should adequately reflect the response of Type 304 stainless steel to similar conditions.

Aqueous corrosion testing consisted of exposure of metal samples to three different aqueous corrosion environments. Samples were exposed

for 1, 8, and 16 yr to constant immersion in seawater and lake water. Samples were also subjected to intermittent immersion in seawater by mounting the samples at the mean tide level. Redundant samples were employed to permit removal of representative specimens at the time intervals listed. A summary of the results of this study [53] is presented in Table 3. Note that all seawater immersion samples perforated at 1 yr or less.

Figure 17 shows a comparison of the corrosion rate as a function of exposure time for Type 302 stainless steel (similar in composition to Type 304 stainless steel) immersed in seawater, immersed in lake water, and intermittently immersed in seawater at the mean tide level. Note that there was no measurable corrosion of the specimen immersed in lake water over the entire 16-yr duration of the experiment. The sample intermittently immersed in seawater exhibited moderate corrosion ($5.00\text{--}2.58\text{ }\mu\text{m/yr}$), while the sample continuously immersed in seawater suffered significant corrosion ($36.25\text{--}14.62\text{ }\mu\text{m/yr}$).

Similar corrosion behavior was noted for Type 316 stainless steel exposed to the same environment, as shown in Fig. 18. There was no measurable corrosion of the sample immersed in lake water. There was slight corrosion in the sample

intermittently immersed in seawater. Significant corrosion ($14.99\text{ }\mu\text{m/yr}$) was noted initially in the Type 316 stainless steel sample immersed in seawater. This corrosion rate decreased over the course of the exposure to $1.25\text{ }\mu\text{m/yr}$ after 16 yr.

The significant differences in corrosion rates indicated for Types 302 and 316 stainless steels in the three aqueous environments are direct results of the effect of chloride ions on the stability of the passivation layer, as outlined in Sec. 2.2. The samples immersed in lake water showed no signs of corrosion, since the chloride ion concentration of the lake water was very low, approximately 50 ppm. The samples that were intermittently immersed in seawater suffered some breakdown of the passivation layer due to chloride attack. However, when the samples were exposed to air during low tide, the passive layer had the opportunity to repassivate in the oxidizing environment of the atmosphere. Hence, the corrosion rate noted for the samples that were totally immersed in seawater was significantly greater than that noted for the intermittently immersed samples.

The addition of molybdenum as an alloying element in austenitic materials has been found to improve the resistance of the passivation layer to chloride ion attack, as mentioned in Sec. 2.2. This behavior is highlighted by a comparison with the

Figure 17. Aqueous corrosion rate of Type 302 stainless steel exposed to seawater, intermittent seawater, and lake water environments [53].

Figure 18. Aqueous corrosion rate of Type 316 stainless steel exposed to seawater, intermittent seawater, and lake water environments [53].

corrosion behavior noted above, as shown in Fig. 19. This figure indicates the variation in corrosion rate as a function of time for Types 302 and 316 stainless steels continuously and intermittently exposed to seawater. Note the significant reduction in corrosion rate for Type 316 stainless steel for the continuously immersed samples. A similar, though less dramatic, improvement in corrosion resistance is noted for the intermittently immersed samples. This reduction in corrosion rate is a result of the improved resistance, afforded by the addition of molybdenum, of the passivation layer to chloride ion attack.

Another aqueous corrosion study employing seawater exposures was completed by Bomberger et al. [59]. In this study, Types 302 and 316 stainless steels were exposed to stagnant and flowing seawater at Kure Beach, North Carolina, for up to 4.5 yr. The results of this study are summarized in Table 3. Both Types 302 and 316 stainless steels suffered pitting and crevice corrosion attack in static and flowing seawater. The corrosion rate for Type 302 stainless steel was 3.71 $\mu\text{m}/\text{yr}$ in stagnant seawater and 2.03–3.71 $\mu\text{m}/\text{yr}$ in flowing seawater. Slightly higher corrosion rates were noted for Type 316 stainless steel under identical

conditions. The corrosion rate for Type 316 stainless steel in stagnant seawater was 6.11 $\mu\text{m}/\text{yr}$, and the corrosion rate in flowing seawater ranged from 1.55 to 6.11 $\mu\text{m}/\text{yr}$. The pitting and crevice corrosion attack of these austenites is typical for seawater immersion tests.

The effects of deep-ocean environments on metal corrosion were addressed in a study by Wheatfall [61]. This study, the results of which are summarized in Table 3, reported on exposures of Type 304 stainless steel and Alloy 825 in seawater at depths to 5640 ft for up to 2.00 yr. Initial short-term exposures (0.34 yr) of Type 304 stainless steel and Alloy 825 indicated no pitting on the exposed surfaces of either alloy. However, significant crevice corrosion was noted in Type 304 stainless steel samples, but little crevice corrosion was observed in Alloy 825. Longer test periods (2.92 yr) under similar conditions resulted in significant pitting in Type 304 stainless steel and scattered pitting in Alloy 825. The measured corrosion rates for Type 304 stainless steel in the long-term exposures was 38.83 $\mu\text{m}/\text{yr}$. The corrosion rate for Alloy 825 under identical conditions was 10.73 $\mu\text{m}/\text{yr}$. Exposure tests lasting 1.06 yr were also completed at the surface of the

ocean for each alloy. Type 304 stainless steel exhibited a corrosion rate of $14.37 \mu\text{m}/\text{yr}$, and Alloy 825 had a corrosion rate of $1.01 \mu\text{m}/\text{yr}$. The dominant mechanism of attack in both alloys was pitting. This study indicated that there are no major differences in the mechanisms or rates of corrosion as a function of depth in an ocean environment.

Lennox et al. [64] studied the effect of cathodic polarization on crevice corrosion in quiescent seawater. This study also included some data on corrosion of Types 304 and 316 stainless steels in seawater without cathodic protection. Both alloys suffered significant crevice corrosion with no cathodic protection. The data on pitting corrosion for these alloys yielded somewhat contradictory results. The corrosion rate due to pitting corrosion after an exposure time of 1.34 yr was $56.76 \mu\text{m}/\text{yr}$ for Type 304 stainless steel and $18.92 \mu\text{m}/\text{yr}$ for Type 316 stainless steel. After a 1.78-yr exposure, the corrosion rate due to pitting was $14.28 \mu\text{m}/\text{yr}$ for Type 304 stainless steel and $57.14 \mu\text{m}/\text{yr}$ for Type 316 stainless steel. This variation in corrosion rates due to pitting attack emphasizes the difficulty in quantifying the localized corrosion behavior of stainless steels.

Studies of corrosion have also been completed on austenitic alloys of interest in geothermal waters. Hong and Pitt [62] studied the corrosion of Type 316L stainless steel and other alloys in Utah geothermal waters. This study employed geothermal water that contained chloride ions at a concentration of $615 \text{ mg}/\text{l}$. A variation in the corrosion rate as a function of water temperature was noted for Type 316L stainless steel. The peak corrosion rate of $63.37 \mu\text{m}/\text{yr}$ was observed at a temperature of 60°C . A summary of the corrosion rates at various temperatures for Type 316L stainless steel in geothermal water is presented in Table 3. The dominant corrosion mechanism for Type 316L stainless steel in this study was pitting.

Another study of the effects of chloride ion concentration on the corrosion of Types 304 and 316 stainless steels in natural waters was completed by Kain et al. [63]. Crevice corrosion of Types 304 and 316 stainless steels was studied in Colorado River water with various chloride ion concentrations ($100\text{--}1000 \text{ mg}/\text{l}$). The effect of surface preparation was also addressed in this study. As indicated in the results summarized in Table 3, there was significant pitting attack in Type 304 stainless steel specimens exposed to Colorado River water, with varying chloride ion concentrations for up to 0.50 yr. The most severe

attack occurred in a sample that was cleaned with a silicon carbide abrasive prior to exposure to water having a chloride ion concentration of $300 \text{ mg}/\text{l}$. The corrosion rate for this sample was $533 \mu\text{m}/\text{yr}$. Significantly less corrosive attack was noted in samples exposed to river water in the as-received condition, which suggests that the passive layer is still intact at the beginning of the experiment in the samples that were not subjected to the silicon carbide cleaning procedure. Samples of Type 316 stainless steel subjected to similar exposures of Colorado River water (with chloride ion concentrations ranging from 100 to $1000 \text{ mg}/\text{l}$) showed no crevice corrosion or pitting attack in any exposure. This result highlights the beneficial effect of molybdenum on the resistance to chloride ion attack.

Oldfield and Sutton [65] have recently attempted to predict the performance of various stainless steels in aqueous chloride-containing environments. The method uses computer analysis of a mathematical model, combined with experimental polarization studies, to predict corrosion in various steels. A critical crevice solution concentration of chloride ions was calculated to be 2.5M for Type 304 stainless steel and 4.0M for Type 316 stainless steel. Adaptation of this work might enhance the capabilities of modeling and prediction necessary to meet verification requirements in the application for a repository license.

One final area of data that was identified in the technical literature and which might be directly applicable to repository conditions is the corrosion of the austenitic alloys in high-temperature water and superheated steam [28, 67, 68]. Early studies by Powell and Von Lossberg [67] and Grabowski [68] identified the effects of dissolved oxygen on the corrosion of internal surfaces in high-pressure boiler tubes. Subsequent work by Wozaldo and Pearl [28] quantified the corrosion of Type 304 stainless steel and Alloy 825 exposed to superheated steam at 566°C (839 K) and 621°C (895 K) for 1.13 yr. The results of this study are presented in Figs. 20 and 21. Figure 20 shows weight loss as a function of time for Type 304 stainless steel exposed to superheated steam at 566 and 621°C . Note that there is a significant increase in corrosion rate with increasing temperature. Also note that in both exposures the weight loss appears to be linear with temperature.

Similar results from Wozaldo and Pearl [28] for Alloy 825 exposed to superheated steam at 566 and 622°C are presented in Fig. 21 for

Figure 19. Comparison of seawater corrosion rates for Types 302 and 316 stainless steels with constant and intermittent immersion [53].

exposure times up to 10,000 hr (1.14 yr). Note that the weight loss as a function of time appears to be approaching saturation after an exposure time of 10,000 hr. Understanding the behavior of Alloy 825 at high temperatures might be helpful (through the use of dimensional analysis and similitude) in modeling the long-term, low-temperature behavior of this alloy under repository-relevant conditions.

A review of the high-temperature work suggests that the oxidation of Type 304 stainless steel results in an oxide film that offers little resistance to further oxidation at high temperatures. Wozaldo and Pearl [28] predict a corrosion rate for Type 304 stainless steel of 256 $\mu\text{m}/\text{yr}$ at 622°C for a 20-yr exposure. However, a similar prediction for the behavior of Alloy 825 results in a corrosion rate of 15.2 $\mu\text{m}/\text{yr}$ at 622°C for a 20-yr exposure. This difference is due to the fact that Alloy 825 forms an adherent, nonporous oxide film at these temperatures.

3.5 Archaeological Metallurgy

One of the tasks of the NWMP is the identification of a metal barrier material that will remain relatively intact for up to 1000 yr under repository

conditions. Selection of such a material would be greatly simplified if there existed a performance data base with examples of component lifetimes similar to the required lifetime of the metal barrier. This is not possible for the austenitic candidate materials. As mentioned in Sec. 3.1, austenitic stainless steels were initially developed about 75 yr ago, and Alloy 825 was developed approximately 50 yr ago; hence, data bases on long-term performance do not exist for these materials.

Though not specifically applicable to the austenitic candidate materials, there are cases in archaeological metallurgy that might enhance the potential for selection of an iron-based alloy. One example of an iron structure that has survived for a significant time is the Delhi Pillar [69]. The Delhi Pillar was erected in about the fourth century A.D. and stands about 22 ft high, with a circumference that varies from 12.5 in. at the top to 16.5 in. at the base. It was constructed of several smaller pieces of nodular cast iron that were hammer-forged together. In 1963, the pillar was relatively corrosion free, with the scale thickness less than 1 μm . However, the bottom portion of the pillar (1–2 ft) was deeply pitted. The 1600-yr lifetime of the pillar is attributed to the extremely dry climate of the region and possibly to the chemical composition of the metal. Though Delhi

Figure 20. Weight loss of Type 304 stainless steel in superheated steam [28].

Figure 21. Weight loss of austenitic Alloy 825 in superheated steam [28].

receives 15 to 30 in. of rainfall annually, most of which falls in July through September, the relative humidity exceeds 80% only about 5% of the time.

Chemical composition might also have a significant impact on the longevity of the pillar. The pillar is constructed of relatively high-purity iron (99.72%), with low concentrations of carbon (0.08%), sulfur (0.006%), and silicon (0.046%), and a relatively high concentration of phosphorus (0.114%). This composition might have resulted in the formation of a protective oxide layer that limited the corrosion of the pillar.

One final aspect of the pillar environment that would impact pillar lifetime is the lack of atmospheric pollution. This probably had a significant impact on the survival of any protective oxide layer that formed on the pillar. The relatively clean, dry environment most likely had the greatest impact on the longevity of the Delhi Pillar.

One final example of archaeological metallurgy of iron-based materials that highlights

longevity is Damascus steel [70]. This is the metal from which Damascus swords were produced in Damascus, Syria, during the Middle Ages (500–1500 A.D.). These swords were fabricated from wootz steel that was formed from malleable iron. The iron was manufactured in a bellows charcoal furnace by heating together magnetite iron and charcoal. Nonmetallic impurities were removed from the ore by repeated hot working. The final product, wootz steel, was made by removing excess carbon from the metal by reheating the metal to a temperature just below the melting point. Careful metalworking, shaping, and heat treatment produced a steel blade so fine that the sword could be bent from point to hilt without breaking or deforming the blade.

These two examples from archaeological metallurgy imply that iron-based alloys can survive for centuries with satisfactory corrosion properties. The composition, heat treatment, and environment are extremely important factors in determining the lifetime of the material.

4. Ranking of the Austenitic Candidate Alloys

Considering only the effects of oxidation and corrosion on the austenitic candidate materials, the following ranking is proposed:

1. Alloy 825
2. Type 316L stainless steel
3. Type 304L stainless steel

This order is based primarily on the corrosion rates observed during seawater exposures. Alloy 825 exhibited the lowest corrosion rate (1.01 $\mu\text{m}/\text{yr}$) for a 1-yr exposure to seawater. Type 316 stainless steel corroded at a rate of

14.99 $\mu\text{m}/\text{yr}$, and Type 304 stainless steel exhibited a corrosion rate of 36.25 $\mu\text{m}/\text{yr}$.

There was little observed difference in the corrosion rates of the austenitic candidate alloys in atmospheric exposures. Exposure to the marine environment at Kure Beach, North Carolina, resulted in a corrosion rate of about 0.025 $\mu\text{m}/\text{yr}$ after an initial transient period. Other atmospheric corrosion environments (i.e., rural and industrial) resulted in corrosion rates that were lower than those in the marine atmospheric environments.

Part 2: Copper-Based Candidate Materials

5. Corrosion of Copper-Based Alloys

5.1 Introduction

As a member of the noble metal group, copper is relatively unreactive as compared with most other metals. Its corrosion resistance and

mechanical properties can often be enhanced by alloying with certain elements. These different copper alloys offer better performance under different corrosive environments. This section contains a limited review of the literature for data on

corrosion that might be relevant to repository conditions. The copper-based alloys of interest to the NNWSI Project are CDA 102 (oxygen-free copper), CDA 613 (7% aluminum bronze), and CDA 715 (Cu-30Ni). The alloy compositions are listed in Table 4.

For the first 100 yr in the repository, many of the containers are expected to be above the boiling temperature of water. Initially, the emplaced containers might be subjected to a humid environment caused by vaporization of entrapped water in the surrounding rock. With time, though, the water-vapor content of the repository atmosphere should decrease until the containers cool and water ingress into the repository can occur. Under normal conditions, water vapor is less oxidizing (less corrosive) than is oxygen to copper. In the radiation environment of the repository, though, gas-phase reactions involving water and other gases, such as nitrogen, will occur and cause the corrosivity of the humid environment to increase. Other gas-phase species (such as O_3 , if present) might also enhance the corrosivity of the environment [71].

For the initial period in the repository, oxide formation will be the dominant form of corrosion (although nitrates may also form). The literature has therefore been surveyed for studies of the oxidation of the alloys in air and pure oxygen. In general, this oxidation is slow at low temperatures and forms a protective layer that inhibits

further oxidation. This protective layer on an alloy often consists of the solute oxide. For the candidate alloys, it would be aluminum or nickel oxides, respectively. This oxide layer might be beneficial, as studies have shown that it is more resistant than the unoxidized metal to corrosive environments [48].

At later times, when the repository has cooled, water ingress into the repository might increase; this may be in the form of vapor or liquid. Water itself is not generally corrosive, but it serves as the medium through which corrosive electrochemical reactions initiated by dissolved gases or ionic species in the water can occur. Because of hygroscopic species, such as chlorides, on metal surfaces, water-vapor condensation can occur at relative humidities of less than 100%. Water-vapor condensation has been reported at 80% relative humidity [72].

In the repository, two additional factors might influence the corrosion rate. The first is that salt deposits might form on the container surface by the evaporation of dripping water from the hot container or by dissolution in a smaller amount of water of salts previously left behind in the rock by distillation. When resolvated, concentrated chloride salts will enhance the electrochemical action of the vadose water. Carbonate deposits, on the other hand, might form a protective layer on the container. The other factor is that, in the radiation environment of the repository, water

Table 4. Compositions of the copper-based candidate alloys (wt%).

Alloy	Cu	Ni	Al	Mn	Sn	Fe	Zn	Other
CDA 102	99.95	—	—	—	—	—	<0.001	Pb < 0.001 Cd < 0.001 S < 0.0018 Hg < 0.0001 P < 0.003
CDA 613	90.82	0.05	6.75	0.16	0.20	2.46	0.01	Pb < 0.01 Co < 0.01
CDA 715	69.18	29.60	—	0.51	—	0.53	0.07	Pb, 0.01 P, 0.002 C, 0.04 S, 0.01

might react with other species (such as N_2 and CO_2) to form acids that might also enhance corrosion.

The following discussion of corrosion of copper alloys is divided into three sections: (1) studies of oxidation in essentially dry air or oxygen, (2) studies of atmospheric corrosion, and (3) studies of aqueous corrosion. Where possible, the corrosion is characterized with respect to the corrosion rate and the corrosive layer formed. Corrosion rates are based on general corrosion, and the corrosion layer is characterized in terms of whether it is exfoliative or adherent and in terms of its composition. The limited data on the degradation of mechanical properties of corroded specimens and on whether localized or pitting corrosion occurred are also reported.

5.2 Oxidation

The initial process of corrosion in the repository is expected to be similar to oxidation in dry air. The corrosion rate and the morphology of the corrosion layer formed will be of utmost interest. The structure of the corrosion layer is important because it might either form a protective layer, which impedes further corrosion, or the layer might exfoliate and offer no resistance to further corrosion. Studies of the oxidation process include studies done both in air and in pure oxygen. Internal oxidation that might occur in the heat-affected zone during welding is discussed in Vol. 8.

Numerous studies have shown that trace amounts of certain gases in the air (on the order of parts per billion) might significantly alter the corrosion process (see Refs. 71 and 73 and references therein). In particular, SO_2 (sulfur dioxide), NH_3 (ammonia), and O_3 (ozone) are quite detrimental to copper. Most laboratory experiments in air do not mention the trace impurity content of the laboratory air. Surface conditions can also affect corrosion rates in that a smooth, polished surface oxidizes more slowly than does a rough surface. Comparative interpretation of experimental results from different studies should be made cautiously.

In this volume, corrosion rates are given in micrometers per year ($\mu m/yr$). Corrosion rates in the literature are reported in terms of penetration depth (e.g., $\mu m/yr$ or $mils/yr$) or weight loss (e.g., $\mu g/cm^2/yr$). When given in terms of penetration depth, the corrosion has been assumed to be uniform across the surface. The weight loss

data have been converted by assuming that the film is compact and planar and consists only of Cu_2O . The assumptions in both cases are questionable, as the corrosion rate is dependent on, for example, the surface crystallographic orientation [74, 75] and on the surface condition [76]. In any case, the rates are based on penetration depth, as this is the most commonly given parameter, and it also gives a good indication of the overall corrosion rate. Data on deviations from general corrosion, such as pitting, are included, if they were reported in the literature.

Pure copper corrodes by forming a cuprous oxide (Cu_2O) film that is adherent to the metal surface. Cuprous oxide is a P-type semiconductor that is highly defective, being deficient in cations (Cu^+). Both cations and electrons can move through this defective structure. The copper ions move to the oxide-gas interface, where they are converted to the oxide. Alloying with solid-solution elements such as aluminum and nickel has been found to decelerate corrosion rates. These alloying elements form more stable oxides than those of copper. The oxide films are more impenetrable to ion transport than the copper oxide films and thus inhibit corrosion. The alloys can form complex corrosion structures. Discussions of these structures are given in Secs. 5.3 through 5.5.

5.3 CDA 102

Because CDA 102 is essentially pure copper (99.95%) with a small amount of impurities, studies of oxidation of pure copper are included. Copper oxides are the stable forms of copper in oxygen (CuO : $\Delta G_f^\circ(25^\circ C) = -30.57$ kcal/mole, and Cu_2O : $\Delta G_f^\circ(25^\circ C) = -35.35$ kcal/mole). Although the formation of oxide is favored under repository-relevant conditions, it is the kinetics of the transformations that are important.

The phase diagram for the copper-oxygen system at a pressure of 1 atm and at oxygen concentrations (θ_O) less than or equal to 0.50 atomic fraction is shown in Fig. 22 [77]. Phase diagrams represent equilibrium conditions that might only be approached extremely slowly. This phase diagram indicates that, for all temperatures less than about $375^\circ C$, cupric oxide (CuO) is the stable oxide formed. At $375^\circ C < T \leq 1065^\circ C$, the oxide formed depends on the oxygen concentration. For $\theta_O < 1/3$, Cu_2O is stable; for $1/3 < \theta_O < 1/2$, a mixed phase of Cu_2O and CuO is stable; and at $\theta_O > 1/2$, only CuO is stable.

Figure 22. Phase diagram for copper-oxygen at a pressure of 1 atm [77].

The stability of the copper oxides also depends on the oxygen pressure. Shown in Fig. 23 are the dissociation pressures for Cu_2O and CuO as a function of temperature. The dissociation pressure is defined as that pressure above which the oxide is stable. For temperatures less than 300°C, the dissociation pressure is less than 10 torr [78]; thus, the oxides formed under repository conditions are stable.

In normal atmosphere at ambient temperatures, the outer layers of bulk copper are readily oxidized. After the initial reaction, further oxidation is inhibited because of the slow transport of ionic species and electrons through the oxide layer. At an oxide layer thickness greater than 1000 Å, the thermal transport of Cu^+ ions through the oxide layer is believed to control the rate of oxidation [79]. For the oxide layer to be protec-

tive, it must be adherent. Exfoliative oxides will continually expose unoxidized copper to the atmosphere, and the corrosion rate will not decrease with time.

The oxidation of copper has been studied extensively for several years [76, 79, 80], but primarily at high temperatures to facilitate formation of the oxide layer and for only short periods of time (less than 1 week). The general types of oxidation rate equations were discussed in Sec. 2.1. Briefly, there are five types of rate laws that have been proposed to explain the experimental results:

$m = k_1 t$	linear,
$m^2 = k_2 t$	parabolic,
$m^3 = k_3 t$	cubic,
$1/m = k_4 \log(t/\tau_1 + 1)$	inverse logarithmic, and
$m = k_5 \log(t/\tau_2 + 1)$	direct logarithmic,

Figure 23. Dissociation pressure for various metal oxides [78].

where m is the mass of oxide formed and t is the time of oxidation. The k 's and τ 's are constants with respect to time, but are functions of temperature and oxygen pressure. Additive constants can appear if the reaction has followed a different law during a preceding period. The rate constants, k 's, are assumed to have an Arrhenius-type dependence, that is,

$$k = A \cdot \exp(-E/RT)$$

where A is the pre-exponential, E is the activation energy, R is the gas law constant, and T is the absolute temperature.

Temperature and oxide thickness are the primary parameters that determine which rate law is operative. The above expressions (with the exception of the linear rate law) are all derived from the assumption that the transport of cations or electrons across the growing film begins with the rate-determining step. The linear rate law applies to nonprotective films. The expected sequence for

adherent films begins with the direct logarithmic law for the thinnest films; the inverse logarithmic and cubic laws at low temperatures; and the parabolic law for thick films and at high temperatures.

The experimental dependence of the oxidation rate of copper on temperature is plotted in Fig. 24 [77]. [The plot is actually of $1/n$ vs temperature, where n is determined from the slope of a plot of $\log(m)$ vs $\log(t)$.] At lower temperatures ($<100^\circ\text{C}$), where the oxide film is thin, the oxidation dependence is primarily direct or inverse logarithmic. At higher temperatures ($>500^\circ\text{C}$), the rate is primarily parabolic. The parabolic or cubic rate laws also appear to be operative for oxide thicknesses greater than $10^4 \text{ \AA}$. The cubic rate law is expected to be operative for the film thicknesses investigated. The deviation is thought to be due to the cracking of blisters at a sufficiently frequent rate to give continuous deviations from the cubic rate law. Again, these results are for relatively short periods of time compared with the time requirements of the repository.

Tylecote [80] has studied the oxidation of copper over the temperature range of 200 to 800°C for times up to 100 hr. At long times in

the lower part of this temperature range, the reaction is approximately cubic ($n = 0.35$), with an activation energy of 28.3 kcal/mole and a pre-exponential of $0.025 \text{ g}^3/\text{cm}^6/\text{hr}$. These values are consistent with oxidation rates found by Campbell and Thomas [Ref. 7 in 80] for $100 < T < 256^\circ\text{C}$. Assuming that the cubic rate law holds for all time, the calculated time to oxidize a 1-cm-thick copper sample at 250°C would be $2 \times 10^{12} \text{ yr}$. At these low temperatures, the film was adherent, with only microblisters present. It is interesting that the oxide layer becomes exfoliative in the temperature range of 300 to 350°C , but at higher temperatures ($400\text{--}450^\circ\text{C}$), the film again becomes adherent. The authors claim that this is due to annealing, which reduces the internal stresses.

Studies have shown that, at ambient temperatures, the oxidation of copper is extremely slow. Rates less than $3 \times 10^{-7} \text{ }\mu\text{m/yr}$ have been reported for laboratory air and oxygen. The thin oxidized layer formed at ambient temperature remains adherent. This rate is expected to decrease with time as long as the oxide remains adherent. Although CuO is the stable oxide at ambient temperatures, only Cu_2O formation has been

Figure 24. Oxidation rate law dependence for copper vs temperature [77]. Filled-in data points are for oxide thicknesses greater than $10^4 \text{ \AA}$.

reported. The Cu_2O oxidation to CuO is obviously kinetically limited.

The composition of the oxide layer as a function of film thickness has been studied for commercial copper (99.99%) at 240°C oxidized in air [81]. The overlayer first formed was a cuprous oxide (Cu_2O) film with no cupric oxide (CuO). This condition persisted until the film thickness became greater than $400 \text{ \AA}$, at which point some CuO could be detected. For films with a thickness greater than $800 \text{ \AA}$, CuO could always be detected. (CuO formation occurred because Cu_2O could be oxidized faster than the Cu^+ ion could be transported to the surface.) At an unspecified thickness, the CuO layer could be mechanically separated from the underlying Cu_2O . The thickness of the CuO layer never exceeded $150 \text{ \AA}$, as it becomes exfoliative at greater thicknesses. The times required to obtain these film thicknesses were not reported.

Studies at higher temperatures ($>600^\circ\text{C}$) report similar findings for the composition of the oxide layer [82]. In addition, the formation of cupric oxide increased with increasing oxygen pressure. The oxide layer at high oxygen pressures was also easier to remove than layers formed at lower pressure. The authors assumed that this was due to thicker oxide formation. For thin oxides, the film was extremely adherent and could not easily be removed mechanically.

An interesting phenomenon that occurs during oxidation of copper is the formation of CuO whiskers at temperatures greater than or equal to 250°C . Gulbransen et al. [83] have studied the effect of the whiskers on the kinetics of the copper oxidation in the temperature range of 250 to 450°C . The whiskers had diameters of 150 to $1500 \text{ \AA}$, depending on the reaction conditions. The authors found that whiskers contained less than 1% of the oxygen taken up by the sample and concluded that the whiskers therefore had no

significant effect on the oxidation rate. Under the experimental conditions used, the oxidation rate followed the cubic rate law.

5.4 CDA 613

Very little information is available on the oxidation of aluminum bronzes in dry air. Sanderson and Scully [84, 85] have performed some oxidation experiments at room temperature and 800°C . At room temperature, the authors performed an 8-month study in laboratory air. They found no tarnish on a Cu-7.5Al-2Si alloy, but a pure copper sample was visibly tarnished. Electron diffraction revealed that some Cu_2O did form on the surface. The authors suggested that the lower rate of oxidation for the alloy was due to an amorphous layer of alumina that inhibited the transport of Cu^+ to the gas interface. Performing 12-hr oxidation experiments at 800°C , the authors did see crystalline alumina. At the higher temperature, no comparison of corrosion rates was made with pure copper, but the rates were 65 to 70 times lower than those for a Cu-3Si alloy.

5.5 CDA 715

There is also very little information on the oxidation of the cupronickel alloys [86]. The data are limited to temperatures greater than 300°C . Studies that are primarily morphological have been performed. When oxidized, the cupronickel alloys form an outer layer of copper oxides with an inner layer of NiO . Additions of nickel to copper have been shown to decrease the oxidation rate at elevated temperatures. At 30% nickel, the cupronickel alloy oxidation rate was decreased by a factor of 3 over pure copper [79].

6. Atmospheric Corrosion

6.1 Introduction

In the repository, the container will be exposed to gases other than nitrogen and oxygen. Some of these other gases might be corrosive to copper. Studies of the atmospheric corrosion of copper are reviewed here to characterize corrosion processes that might occur in the repository. In general, most gases that are corrosive to copper

are corrosive only in the presence of water and oxygen.

The corrosion of copper in the atmosphere usually proceeds through many stages. Initially, copper will form a brown tarnish, consisting mostly of sulfides and oxides, which gradually thickens to form a black film. Under most atmospheric corrosion conditions, this black film remains for several years before the green patina

develops. There appears to be a definite incubation period before the transformation to the green patina occurs. Generally, the main constituent of the patina is basic copper sulfate in industrial and rural atmospheres; but in marine atmospheres, basic copper chloride will be found. Basic copper carbonate is not usually a main constituent of the patina. Under the green patina, a red cuprous oxide layer is always present. The patina found on copper alloys will sometimes differ in color from that found on copper due to the effect of corrosion products from the alloying elements.

Atmospheric corrosion at ambient temperatures is generally an electrochemical phenomenon and, as such, it requires that the metal surface be wet and that electrolytes be present in solution. The metal surface might be wetted by rain, dew, sea spray, or water adsorbed from the atmosphere by hygroscopic salts (deposited or formed by corrosion). Hygroscopic salts include calcium and magnesium chlorides [48]. Hygroscopic adsorption will occur when the humidity is greater than the critical relative humidity, which is dependent on the metal and the surface contaminants. The electrolytes can come from adsorption of gas-phase species (e.g., SO_2 , CO_2 , and NO_2) and from chloride ions (Cl^-) in seawater spray. Oxygen, also necessary for corrosion, will readily adsorb into the water film from the air.

Other factors that might affect the corrosiveness of an environment are rain and sunshine [48]. Frequent rain generally reduces corrosion by rinsing off salt and dust residue. When salt and dust contamination is not washed off, metal surfaces might be attacked at a greater rate than exposed surfaces. Solar radiation might stimulate photosensitive corrosion reactions on metals such as copper and iron, and it might also stimulate biological activity such as fungal growth. Fungi and molds mainly increase corrosivity by holding moisture on the metal surface.

The gas-phase species concentrations vary considerably, depending on geographical location [71]. Sulfur oxides (SO_x) primarily originate from the combustion of coal or oil. Industrial and urban areas typically have large deposition rates of sulfur oxides (up to 100–200 mg/m²/day), but rural areas have much smaller deposition rates (10–30 mg/m²/day). Sulfur oxides are particularly corrosive, as evidenced by high corrosion rates in industrial environments. Hydrogen sulfide (H_2S) is also highly corrosive to copper. Nitrogen oxides (NO_x) are formed by electric discharge phenomena or by combustion processes.

The CO_2 concentration in air varies from 0.03 to 0.05 vol%. Dry nitrogen oxides and CO_2 have not been documented as strongly corrosive agents. Chlorides are deposited mainly from seawater spray. In marine environments, the copper corrosion products are primarily chlorides. Ammonia (NH_3), which might come from biological decay, does not attack copper in a dry atmosphere; however, it is extremely corrosive to all copper alloys in moist atmospheres.

The corrosion products formed from copper depend on the particular atmospheric conditions under which the corrosion reaction occurs. Corrosion in pure oxygen or dry air, as discussed above, results in the formation of only copper oxides (Cu_2O and CuO). The oxidation rates are very slow—only on the order of 10^{-7} $\mu\text{m}/\text{yr}$ at ambient temperatures.

In sulfur dioxide (SO_2), the corrosion rate and corrosion products depend on the relative humidity and SO_2 concentration [87]. In the absence of water vapor, sulfur dioxide has no influence on the normal oxidation that takes place at room temperature in dry, pure air, but effects are observed in moist air. One possible mechanism is that, in the presence of a water film, SO_2 is readily absorbed and reacts with the water to form sulfurous acid (H_2SO_3). Then, it reacts with copper to form the metal sulfite, which reacts with oxygen to form the sulfate.

The corrosion rate increases rapidly above a relative humidity of 63% and is strongly dependent on SO_2 concentration, as illustrated in Fig. 25 [87]. The corrosion products are also strongly dependent on the SO_2 concentration. At 1% SO_2 , the film is normal sulfate (CuSO_4); below 1% SO_2 , basic sulfate is formed ($\text{Cu}(\text{OH})_2 \cdot \text{CuSO}_4$); and above 1% SO_2 , the acid salt is formed (HCuSO_4). The basicity of the deposits increases with age and might reach a maximum of 3, i.e., $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ (brochantite). This product (brochantite) is stable and might account for the protective nature of the film of corrosion product.

Other gases in combination with water form corrosion products on copper surfaces [87]. Chlorine or chloride ions react to form basic copper chloride. With aging, a maximum basicity of 3 can be reached, forming atacamite ($\text{CuCl}_2 \cdot 3(\text{OH})_2$). Carbon dioxide (CO_2) and nitrogen oxides react to form basic carbonates and nitrates, respectively. Like the basic sulfates, these corrosion products are very stable and form protective overlayers that inhibit further corrosion.

Figure 25. Relationship between corrosion and concentration of SO_2 in atmospheres of high relative humidity [87].

In contrast to sulfur dioxide, hydrogen sulfide (H_2S) will react with copper in the absence of water. In fact, water vapor inhibits the corrosivity of H_2S . In dry atmospheres, H_2S reacts with copper to form copper sulfides and oxides.

Potential-pH (Pourbaix) diagrams give the thermodynamic possibilities for corrosion and the formation of different corrosion products. The diagram for the $\text{Cu-H}_2\text{O}$ system, shown in Fig. 26 [72], gives the stability regions for various species with respect to the redox potential and the pH value of the corrosive agent. The stability region for water is enclosed between the dashed lines. The borderlines between the solid species and the species in solution depend on the activities (concentrations) of the species in solution. For atmospheric corrosion, the solution species concentrations fluctuate, but they are generally rather high. In spite of the fluctuations, the regions of stability do not radically change because the potential and the pH value are proportional to the logarithm of the concentration. The potential-pH diagrams give information only on the thermodynamic possibilities for reactions and not on the reaction kinetics.

When studying atmospheric corrosion, the effects of trace species in the atmosphere on the potential-pH diagram must be considered. In particular, H_2CO_3 , SO_4^{2-} , Cl^- , and NO_3^- must be

considered because, under certain conditions, they might form solid phases or solution complexes with the corroding metal. In addition, the pH value of the water film for atmospheric corrosion generally ranges from 2 to 7; it is usually more acidic in polluted air.

The potential-pH diagram for $\text{Cu-SO}_4^{2-}\text{-H}_2\text{O}$ at 25°C with 10^{-1} mol/l Cu^{2+} and 10^{-3} mol/l SO_4^{2-} is shown in Fig. 27. In the stability region for water, the copper is in solution at low pH values and remains adherent for pH values above 4. For a portion of $4 < \text{pH} < 6$, basic copper sulfate is formed.

The corrosion products formed as a function of electrolytes can also be displayed on stability diagrams, which are diagrams of the corrosion products as a function of pH and anion content. Stability diagrams for the basic sulfate, carbonate, nitrate, and chloride are shown in Fig. 28. Low pH values favor the dissolution of copper as Cu^{2+} for each of the anions. Basic copper sulfate is predicted to form even for very low concentrations of sulfate anion. Basic copper nitrate formation requires a high concentration of nitrate in solution. The formation of basic copper chloride or carbonate requires anion concentrations that are intermediate between concentrations required for the formation of basic copper sulfate and the nitrate.

Figure 26. Potential-pH diagram; Cu-H₂O, 25°C, 10⁻⁶ M Cu [72].

Figure 27. Potential-pH diagram; Cu-SO₄²⁻-H₂O, 25°C, 10⁻¹ M Cu, 10 M SO₄²⁻ [72].

Figure 28. Stability domains of basic copper salts in aerated aqueous solution with varying anion content and pH values; 25°C, 10^{-1} M Cu [72].

The corrosion rate (kinetics) depends on the amount and composition of the electrolyte on the metal surface. The instantaneous rate may vary with time, but the cumulative attack over a significant period (years) does not depend so strongly on the time of wetness. This is true because, when the surface becomes wet, the large amount of corrosive surface contaminants accumulated during a long dry period will generally cause a higher corrosion rate than the smaller amount accumulated during a shorter dry period. Corrosion rates are initially high but tend to decrease with time because of the formation of a protective oxide layer. In general, corrosion rates of copper in various atmospheres are approximately as follows:

Atmosphere	Corrosion rate (mm/yr)
Rural	0.5
Urban	1 to 2
Marine	1

6.2 Atmospheric Corrosion Tests

This section is a compilation of reported atmospheric corrosion tests. Results are presented for the candidate alloys but, when a study does not include a candidate alloy, a similar alloy is substituted if possible. To facilitate comparison of different test results, all the data have been converted to penetration depth. This, of course, assumes that the corrosion is uniform across the surface which, in some cases, might not be valid, as localized corrosion or uneven corrosion might occur. If test results specified this, it is mentioned here.

With respect to the initial repository-like conditions, tests performed in the tropics offer several advantages over tests performed in temperate climates. In the tropics, temperatures remain relatively constant and warm throughout the year, and high humidity exists for seacoast testing (high humidity might exist in the repository for initial emplacement of the waste containers).

The U.S. Naval Research Laboratory has performed 16-yr atmospheric corrosion tests on numerous metals at two sites in Panama [88]. A coastal site at Cristobal has nearly constant temperature (27°C) and humidity (80%) throughout the year. An inland site at Miraflores also has nearly constant average temperature, but it is relatively dry. The results of corrosion testing (data on general corrosion, pitting, and tensile-strength loss) are presented in Tables 5 and 6 [88]. Generally, the conditions at the seacoast are more corrosive than at the inland sites. The authors reported that the corrosion rates at both sites steadily decreased with time and appeared to have reached steady state at 16 yr. Corrosion rates at 16 yr are all less than or equal to 0.8 $\mu\text{m}/\text{yr}$, with pure copper corroding fastest and the aluminum bronze and the cupronickel corroding at 0.5 $\mu\text{m}/\text{yr}$. Pitting is negligible for all the alloys at both sites. Tensile-strength losses are relatively small, with

pure copper suffering the largest losses at both sites, 2 and 5% at the inland and seacoast sites, respectively.

In 1955, Tracy [89] reported the corrosion results of a 20-yr atmospheric test on copper alloys at various sites in the United States. Data on penetration depth are presented in Table 7 [89], and the percent changes in weight and tensile strength are given in Table 8 [89]. Only broad classifications of the environments are given in the tables. More detailed descriptions of the environments are given in Ref. 89. In this study [89], the cupronickel alloy contained 1% tin and no iron; the aluminum alloy did not contain iron.

The corrosion rates vary from 0.05 to 2.6 $\mu\text{m}/\text{yr}$, depending on the environment. In the dry rural atmosphere of Phoenix, Arizona, no alloy-specific rates were given, but the corrosion rates were extremely slow, 0.05 to 0.2 $\mu\text{m}/\text{yr}$. At the La Jolla, California site, ocean spray is rarely

Table 5. Data on corrosion of noncoupled metal panels exposed at a tropical inland site at Miraflores, Panama [88].

Metal	General corrosion						Pitting ^b			Tensile strength	
	Average penetration (μm)					Final rate ^a ($\mu\text{m}/\text{yr}$)	Average depth (μm)		Deepest (μm)	Percent loss	
	1	2	4	8	16 yr		8	16 yr		8	16 yr
Cu-Al 5	1.0	1.8	2.3	3.3	6.1	<0.3	<125	<125	<125	<1	<1
Cu 99.9	2.0	2.9	3.8	4.8	6.9	<0.3	<125	<125	<125	2	2
Cu 70-Ni 30	0.5	1.3	2.0	3.3	6.9	0.5	<125	<125	<125	<1	1

^aStabilized corrosion rate; the slope of the linear portion of the curve, usually after 2 to 8 yr.

^bAverage of 20 deepest pits with measurable penetrations greater than 125 μm .

Table 6. Data on corrosion of noncoupled metal panels exposed at a seacoast site at Cristobal, Panama [88].

Metal	General corrosion						Pitting ^b			Tensile strength	
	Average penetration (μm)					Final rate ^a ($\mu\text{m}/\text{yr}$)	Average depth (μm)		Deepest (μm)	Percent loss	
	1	2	4	8	16 yr		8	16 yr		8	16 yr
Cu-Al 5	2.0	2.8	3.8	5.8	9.9	0.5	<125	<125	<125	1	2
Cu 99.9	4.3	5.8	9.7	14	20	0.8	<125	<125	<125	4	5
Cu 70-Ni 30	0.8	1.5	3.0	5.8	10	0.5	<125	<125	<125	<1	1

^aStabilized corrosion rate; the slope of the linear portion of the curve, usually after 2 to 8 yr.

^bAverage of 20 deepest pits with measurable penetrations greater than 125 μm .

Table 7. Corrosion rate (penetration depth) determined from weight losses observed in atmospheric tests on copper alloys. Tests were conducted at various sites in the United States for periods of 10 and 20 yr [89].

Alloy	Corrosion rate ($\mu\text{m/yr}$)													
	Altoona, Pa. Industrial		New York, N.Y. Industrial marine		Sandy Hook, N.J. Northern marine		La Jolla, Ca. Severe marine		Key West, Fla. Tropical marine		Phoenix, Ariz. Rural dry		State College, Pa. Northern rural	
	10	20 yr	10	20 yr	10	20 yr	10	20 yr	10	20 yr	10	20 yr	10	20 yr
Cu 99.98	1.3	1.4	1.2	1.3	0.6	—	1.4	1.2	0.5	0.6	0.05–0.2		0.56	0.43
Cu 92.1-Al 7.8	1.8	1.6	1.7	1.5	1.5	1.2	0.2	0.1	0.3	0.05	0.05–0.2		0.15	0.20
Cu 69.1-Ni 28.1- Sn 1.0-Zn 0.6	2.2	2.6	2.1	2.0	1.2	—	0.28	0.30	0.33	0.3	0.05–0.2		0.33	0.48

Table 8. Percent weight loss (WL) and percent change in tensile stress (TS) seen in 20-yr tests of atmospheric corrosion [89].

Alloy	Altoona, Pa. Industrial		New York, N.Y. Industrial marine		La Jolla, Ca. Severe marine		Key West, Fla. Tropical marine		Phoenix, Az. Rural dry		State College, Pa. Northern rural	
	WL	TS ^a	WL	TS	WL	TS	WL	TS	WL	TS	WL	TS
Cu 99.98	6.1	0	6.7	0.3	5.5	3.9	2.8	-3.3	0.9	-0.1	2	-3.3
Cu 92.1-Al 7.8	7.2	0	7.3	—	1.1	0	0.5	0	0.1	0	1.1	0
Cu 69.1-Ni 28.1- Sn 1.0-Zn 0.6	12.2	12.8	12.8	12.2	1.4	5.2	1.3	4.4	0.3	4.4	2.2	1.7

^a Tensile-test samples were cut corrosion plates.

washed off the samples by rain, leading to a situation in which salts can accumulate on the sample surfaces. In this environment, the corrosion rates varied from 0.1 to 1.2 $\mu\text{m}/\text{yr}$, with the aluminum bronze performing best and the pure copper performing worst.

The percentages of tensile-strength loss and weight loss are given in Table 8. Losses in tensile strength are generally less than 10%. In Phoenix, pure copper and aluminum bronze suffered no measurable loss, but the cupronickel alloy suffered a 4.4% loss. In the marine environment of La Jolla, the aluminum bronze again did not suffer any measurable loss, but pure copper had a loss of 3.9%, and the cupronickel alloy had a loss of 5.2%. The data on tensile-strength loss are for corrosion samples cut after the 20-yr test. Tensile-test samples cut prior to corrosion testing showed significantly higher tensile-strength losses after corrosion. Also, one aluminum bronze tensile-test sample suffered dealuminization.

Atmospheric corrosion tests were performed in temperate climates by Costas [90] at four sites in the United States. Two of the sites were marine (Point Reyes, California; and Kure Beach, North Carolina), one was rural (State College, Pennsylvania), and one was industrial (Newark, New Jersey). The data on corrosion rate are reproduced in Table 9 [90]. The corrosion rates appear to have stabilized or decreased at 20 yr, except possibly at the rural site. In general, the worst corrosion took place in the industrial environment and the least corrosion took place in either the marine or rural environments, depending on the alloy. All the alloys behaved quite similarly within a particular environment. Overall, the aluminum bronze performed best, with rates ranging from 0.22 (marine) to 1.4 $\mu\text{m}/\text{yr}$ (industrial).

In general, corrosion products in the marine environments were Cu_2O and basic copper chloride, $\text{Cu}_2\text{Cl}(\text{OH})_3$ (atacamite); in the rural and industrial environments, corrosion products were Cu_2O and basic copper sulfate, $\text{Cu}_4(\text{OH})_6\text{SO}_4$ (brochantite). In the marine environment, the alloys were found to retain greater amounts of the corrosion product. Pitting was not significant with any of the alloys. Intergranular attack did occur in the aluminum bronze alloy at all sites except Point Reyes.

Tensile strength losses were generally less than 5% except for that of the aluminum bronze alloy in the industrial environment, where the alloy suffered intergranular attack and tensile-strength losses were about 6%.

The Statue of Liberty in New York Harbor can be viewed as a long-term study of the atmospheric corrosion of copper [91]. The copper content of the statue generally ranges from 95 to 98%, with some sections having significant zinc content. Although the thickness of the skin of the statue varied, it was generally 0.25 cm. Before the refurbishing of the statue in the 1980s, the corrosion rates at different locations on the statue were found to vary from 1.6 to 0.8 $\mu\text{m}/\text{yr}$, with the horizontal sections corroding the most rapidly. These values are typical for copper corrosion in marine environments. There were areas where abnormally severe corrosion occurred, such as areas where aqueous liquid collected because of improper drainage or areas where aqueous runoff caused erosion corrosion of the copper. Some pitting was observed, but it occurred in areas that had significant zinc content.

The corrosion layer consisted of a CuO underlayer and a mixed copper sulfate overlayer. The overlayer composition varied according to exposure conditions. In sheltered areas

Table 9. Corrosion rates determined in tests in temperate climates for periods of 2, 7, and 15 or 20 yr [90].

Alloy	Corrosion rate ^a (mm/yr)										
	Kure Beach, S.C. Eastern marine			Newark, N.J. Industrial			Point Reyes, Ca. Western marine		State College, Pa. Rural		
	2	7	20 yr	2	7	20 yr	2	15 yr	2	7	20 yr
Cu 98.7-Sn 1.18	2.1	1.8	1.1	1.7	1.6	1.4	1.1	0.38	0.84	0.64	0.65
Cu 91.65-Al 6.4-Si 1.85	0.43	0.43	0.46	1.1	1.3	1.2	0.23	0.22 ^b	0.28	0.33	0.54
Cu 77.18-Al 22.76	0.91	0.79	0.77	0.48	1.5	1.5	0.61	1.0	0.48	0.48	0.70

^aCorrosion rates were determined for three samples.

^bOnly two specimens were analyzed, and there was a large scatter in the corrosion rates.

Table 10. Typical indoor and outdoor ranges of inorganic pollutants [73].

Pollutant gas	Typical outdoor range ($\mu\text{g}/\text{m}^3$)	Typical indoor range ($\mu\text{g}/\text{m}^3$)
SO ₂	3–185	1–40
NO ₂	20–160	3–60
O ₃	10–90	7–65
HCl	0.3–5	0.08–0.3
Cl ₂	<5% of HCl except where a local Cl ₂ source exists	0.004–0.015
NH ₃	6–12	10–150

unaffected by wind and aqueous runoff and in areas not directly facing Manhattan, the patina was thicker and was composed predominantly of basic copper sulfate (brochantite). In areas facing Manhattan, the patina was thinner and was composed of both brochantite and antlerite. Antlerite is more susceptible to erosion and is thought to form because of acid deposition from Manhattan and inland power plants.

As a point of reference for conducting laboratory experiments on corrosion, it is of importance to mention the differences reported between indoor and outdoor corrosion rates. Rice et al. [92] have made such a comparison of several metals, including copper, at several sites throughout the United States. The corrosion rates of copper were at least 100 times greater outdoors than they were indoors. In general, the copper corrosion rate decreased with time for the indoor corrosion. The corrosion products were complex combinations of copper hydroxide, chloride, sulfate (sulfite), carbonate, and nitrate. The authors attributed the decreased corrosion rates to the lower concentration of pollutants and lower relative humidity indoors than outdoors.

Rice et al. [73] have studied the effect of controlled atmospheres on the corrosion of copper. As a point of comparison, typical indoor and outdoor concentrations of the pollutant studied (in the year 1981) are given in Table 10 [73]. In two synthetic polluted atmospheres (shown in Table 11 [73]), the corrosion of copper is highly dependent on relative humidity, as shown in Fig. 29 [73]. The corrosion rate increases by a factor of 8 as the relative humidity increases from

30 to 80%. This finding indicates the electrochemical nature of the atmospheric corrosion of copper, with the water-pollutant chemistry providing the medium for ionic mobility and surface product dissolution.

The general corrosion rates of copper as a function of various pollutant concentrations at 70% relative humidity are shown in Table 12 [73]. In particular, copper corrosion was very sensitive to sulfur dioxide (SO₂), hydrogen sulfide (H₂S), ozone (O₃), hydrogen chloride (HCl), and chlorine (Cl₂). Copper corrosion was less sensitive to ammonia (NH₃) and nitrogen dioxide (NO₂). (In some atmospheres, e.g., ammonia, copper alloys are susceptible to stress corrosion cracking, a localized form of corrosion; this type of corrosion is discussed in Vol. 4.)

Table 11. Composition of laboratory test environments ($T = 25^\circ\text{C}$) [73].

Pollutant gas	Concentration	
	Environment A ($\mu\text{g}/\text{m}^3$)	Environment B ($\mu\text{g}/\text{m}^3$)
SO ₂	810	860
NO ₂	940	990
O ₃	334	0
NH ₃	0	0
Cl ₂	8.6	8.4
HCl	0	16.8
H ₂ S	21	54

Table 12. Summary of rates of corrosion of copper determined at various pollutant concentrations [73]. Tests were performed at 70% relative humidity and 25°C. For each pollutant, the first row gives the pollutant concentration in $\mu\text{g}/\text{m}^3$, and the second row gives the copper corrosion rate in $\mu\text{g}/\text{cm}^2/\text{hr}$. The third row is the corrosion rate in $\mu\text{m}/\text{yr}$. The columns n and A give the coefficients in the expression $r = AC^n$, where C is the pollutant concentration. The column CC gives the correlation coefficient, which represents the quality of the fit of the data to the analytic expression.

Pollutant	Concentration ($\mu\text{g}/\text{m}^3$) Corrosion rate ($\mu\text{g}/\text{cm}^2/\text{hr}$) Corrosion rate ($\mu\text{m}/\text{yr}$)					n	A	CC
SO_2^a	0	39	118	786	1415			
	0.56	0.87	1.08	2.62	2.76	0.36	0.22	0.99
	5.48	8.50	10.55	25.6	27.0			
SO_2^b	50	152	299					
	0.0042	0.0063	0.0075			0.33	0.001	0.996
	0.041	0.062	0.073					
H_2S^a	0	7.9	20	66	328			
	0.77	1.24	1.68	1.88	4.08	0.30	0.63	0.97
	7.53	12.1	16.4	18.38	39.9			
H_2S^b	2.62	6.50	14.4					
	0.0026	0.0032	0.013			0.93	0.00087	0.90
	0.025	0.031	0.13					
H_2S^c	4.42	11.6	22.4					
	0.039	0.050	0.071			0.36	0.022	0.98
	0.38	0.49	0.69					
Cl_2^a	0	87	29	116	290			
	1.26	1.21	1.43	1.22	1.27	0	1.29	0
	12.3	11.8	14.0	11.9	12.4			
Cl_2^b	7.83	16.5	25.2					
	0.113	0.166	0.244			0.64	0.029	0.99
	1.10	1.62	2.38					
Cl_2^d	70	11.9	20.3					
	0.060	0.15	0.216			1.20	0.0063	0.97
	0.58	1.47	2.11					
HCl^b	2.47	4.93	7.40					
	0.065	0.10	0.13			0.63	0.037	0.999
	0.63	0.98	1.27					
NO_2^a	0	26	102	376	1316			
	1.15	1.18	1.41	1.46	1.78	0.097	0.87	0.97
	11.24	11.5	13.78	14.27	17.4			
O_3^a	3	27	98	330	980			
	0.26	0.47	0.75	1.62	1.15	0.29	0.20	0.85
	2.54	4.60	7.33	15.8	11.24			
NH_3^a	0	2.1	6.7	35	139			
	1.59	1.99	1.77	1.75	1.48	-0.06	2.67	0.94
	15.54	19.45	17.3	17.11	14.47			

^aReference environment was A in Table 11.

^bNo other pollutants were present.

^cHCl gas was present at $1.46 \mu\text{g}/\text{m}^3$.

^d SO_2 gas was present at $47 \mu\text{g}/\text{m}^3$.

Figure 29. Corrosion rate of copper and silver vs relative humidity in two synthetic polluted atmospheres [73]. Atmospheres are given in Table 11.

7. Aqueous Corrosion

Section 6 discussed atmospheric corrosion and highlighted the fact that the operative corrosive process on copper and its alloys is primarily electrochemical. An aqueous environment therefore represents a more corrosive environment for the metals. Under most circumstances, seawater is more corrosive than fresh water (because of the higher salt content). Copper and its alloys have been used extensively in marine applications. The alloys have been proposed and are used for materials in desalinization processes [93] and in heat exchangers [94–97] in marine environments. The cupronickel alloys, in fact, are used extensively in these applications.

The U.S. Naval Research Laboratory has performed 16-yr corrosion damage studies on numerous metals in aqueous environments in the

tropics [53]. The metals studied included pure copper, Cu-30Ni, and a 5% aluminum bronze, and the results are reproduced in Table 13 [53]. These alloys are the same as those used in the study of atmospheric corrosion discussed in Sec. 6.2 [88]. Three different environments were used: (1) complete immersion in the Pacific Ocean; (2) intermittent immersion in the Pacific Ocean (sample at mean tide positions); and (3) complete immersion in Gatun Lake, which is : : water lake (solids 50 ppm).

The complete immersion in seawater was the most corrosive condition, with the corrosion rates at 16 yr for the three alloys falling between 2.3 and 2.5 µm/yr. The intermittent seawater immersion and the fresh water immersion corrosion rates were the same for each alloy. The

Table 13. Data on corrosion damage for copper alloys exposed in aqueous environments [53].

Metal ^a	Envir. ^b	General corrosion ^c				Pitting penetration (μm/yr)			
		Avg penetration (μm)			Final rate ^d (μm/yr)	Avg of 20 deepest pits ^e			Deepest pit ^f (μm)
		1 yr	8 yr	16 yr		1 yr	8 yr	16 yr	
Cu 70-Ni 30	S	12.7	38.1	58.4	2.5	<127	<127	<127	940
	M	2.5	10.2	20.3	1.0	<127	<127	<127	<127
	L	5.1	25.4	33.0	1.0	<127	<127	<127	<127
Cu 99.9	S	30.5	134.6	152	2.29	508	711	787	1450
	M	17.8	27.9	33.0	0.51	<127	254	<127	584
	L	5.1	20.3	25.4	0.51	<127	<127	<127	<127
Aluminum bronze (5% aluminum)	S	5.1	20.3	33.0	2.5	<127	<127	<127	533
	M	2.5	10.2	15.2	0.5	<127	<127	<127	<127
	L	2.5	7.6	10.2	0.5	<127	<127	<127	<127

^aAll samples were degreased before exposure.

^bS, seawater immersion; M, seawater mean tide; L, lake water immersion.

^cValues were calculated from weight-loss data.

^dSlope of the linear portion of the time-corrosion curve, or if nonlinear, the slope of the tangent at 16 yr.

^eTwenty-pit average was determined from the five deepest pits on duplicate panels.

^fThe deepest single pit during the 16-yr exposure.

cupronickel alloy had the highest corrosion rate at 16 yr (1 μm/yr), and the other two alloys had rates that were about half of the cupronickel rate.

The pitting susceptibility of the pure copper is much higher than that of either of the other two alloys. Although all the alloys pitted in seawater, the deepest pit after 16 yr occurred in pure copper (1450 μm), followed by the copper-nickel alloy (940 μm), and then the aluminum bronze (533 μm). Only pure copper pitted significantly for the intermittent immersion in seawater (deepest pit in 16 yr was 584 μm). There was no significant pitting for any of the alloys in the fresh water test.

Although the U.S. Naval Research Laboratory did not perform an analysis of the layer of corrosion product, other studies have shown that, in seawater immersion, the film often contains deposits on top of the cuprous oxide layer. These deposits might be cupric oxychloride, cupric hydroxide, or basic copper carbonate and calcium carbonate [48], and are thought to impede further corrosion.

Tests with seawater at elevated temperatures have also been performed, and the results show that the corrosion rate decreases as the temperature increases (see Fig. 30). The authors [48] attributed the less aggressive environment and the decreased corrosion rate to both the reduced oxy-

gen content and the greater tendency to form mineral scale on the surface. These authors have also shown that oxygen content is an extremely important factor influencing the corrosiveness of seawater.

Copper-nickel alloys are frequently used in seawater-cooled heat exchangers, and they generally give satisfactory performance. Both Cu-30Ni and Cu-10Ni were developed during the 1930s and 1940s in the United States and the United Kingdom [98]. These cupronickel alloys have been used extensively in tubing in steam-heat exchangers. As a consequence, numerous corrosion studies have been performed in wet atmospheres.

Castle et al. [99] compared the oxidation of Cu-30Ni to that of copper under a variety of conditions, in particular, in atmospheric oxygenated steam at 300°C. With thermal cycling to 95°C once every day, the Cu-30Ni corrosion rate was 3.6 μm/yr or less at 50 days. The cumulative copper corrosion was similar over the first 45 days, although the rate at 40 days appeared to be greater for copper. The corrosion layer, which was adherent, consisted of an outside layer of Cu₂O and an inside layer of mixed Cu₂O and NiO. Castle et al. [99] also studied the oxidation under a variety of other conditions and found significantly different corrosion layers and oxidation rates. Oxidation in pure oxygen at 300°C was

Figure 30. Effect of temperature on corrosion rate of copper-based heat exchanger tube materials in deaerated seawater [48].

significantly slower than in aerated steam atmospheres at 300°C.

Swartzendrüber and Bennett [100] have studied the effect of iron concentration on the corrosion rate of Cu-10Ni in 3.5% NaCl solution at 70°C. The samples were moved in the bath at a rate of 0.4 m/s. Swartzendrüber and Bennett found that, for iron to effectively decrease the corrosion rate (by up to a factor of 2), the iron must be in solid solution. Iron precipitates were thought to act as local anodes that enhanced the corrosion rate. From Mossbauer spectroscopy, the authors suggested that the precipitates were face-centered cubic (fcc) iron-nickel, with 30 at.% nickel.

Francis [98] studied the effect of temperature on the corrosion rate of Cu-30Ni subjected to impingement attack of seawater. The corrosion rate decreased by a factor of 2.5 with a temperature increase from 0 to 15°C. Concomitant with the decrease in corrosion was an electropositive increase of more than 100 mV in the corrosion potential with the temperature increase. Francis presented evidence to indicate that the increased corrosion resistance was due to the incorporation of iron in the corrosion film. In contrast, in the study of Swartzendrüber and Bennett [100], it was found that the corrosion rate decreased when the iron content was increased to 2%. A possible difference in these findings was that the manganese concentration was higher in the latter study; some unknown synergistic effect of manganese might be responsible for this result.

Efird [101] studied the effect of iron concentration on the corrosion resistance of copper-nickel alloys. In Cu-30Ni, an iron concentration of about 0.7 wt% gave corrosion rates of about 3 µm/yr (2-yr test). In agreement with Francis, Efird found an electropositive shift of more than 100 mV in the corrosion potential for a solid-solution iron concentration above 0.8% in the alloy. For corrosion in quiescent seawater, increasing the iron content above 1% increased the corrosion rate by about a factor of 2.

Syrett [102] studied the effect of sulfide-polluted seawater on the corrosion of Cu-10Ni. Sulfide in unaerated seawater corroded Cu-10Ni at approximately the same rate as in aerated, unpolluted water. In contrast to aerated, unpolluted water (which formed a protective cuprous oxide layer), the sulfide-polluted water formed an underlayer of cuprous oxide, but it was covered with porous copper sulfide. Upon substituting unpolluted, aerated seawater for the polluted water, Syrett found that the corrosion rate increased and the sulfide layer was removed. Eventually, the corrosion rate returned to the rate characteristic of unpolluted, aerated water. The author also pointed out that the corrosion product layer in aerated seawater is usually Cu_2O , but $Cu_2(OH)_3Cl$ is frequently found; CuO , $Cu(OH)_2$, $CuCl_2$, $Cu_3(OH)_2(CO_3)_2$, and $CaCO_3$ have also been found [102 and references therein].

8. Other Corrosive Environments and Degradation Modes

The previous sections have dealt with general oxidation, atmospheric corrosion, and aqueous corrosion. Sections 8.1 through 8.3 briefly discuss the corrosion of the candidate copper alloys in specific corrodents: acids, alkaline solutions, and neutral solutions [103, 104].

8.1 Acids

The high-copper alloys are usually more resistant to acid corrosion than is copper, but all have the same order of resistance. Aeration of acid solutions, in general, enhances the corrosiveness of the solution. Aeration is particularly necessary for low-concentration acid solutions. Increasing the temperature of an acid solution usually increases its corrosivity except that, at high temperatures, the solubility of oxygen might be so low that corrosion rates decrease. The formation of low-solubility corrosion products reduces corrosion rates. Fluid motion can also enhance corrosion by removing copper ions that otherwise would remain close to the surface of the metal and form a polarizing film. Also, dealuminification of aluminum bronzes containing more than 8% aluminum can occur in acid solutions. Oxidizing salts (such as ferric, cupric, and stannic salts) are themselves corrosive, and they also enhance the corrosivity of acids. Other oxidizing salts (such as permanganates, chromates, and chlorates) require the presence of acid to be highly corrosive, or can accelerate the corrosive action of acids.

8.1.1 Nitric Acid

Nitric acid is an oxidizing acid and as such is highly corrosive to copper and its alloys. Copper corrodes at a rate of $76 \mu\text{m}/\text{yr}$ for quiet submersion in 0.06% acid. Other copper alloys corrode similarly. Nitrous acid, which is a by-product of the corrosion, accelerates the rate of attack. Aeration is not necessary for the corrosivity of nitric acid.

8.1.2 Hydrochloric Acid

Hydrochloric acid is the most corrosive of the nonoxidizing acids to copper alloys. At room temperature, copper corrodes at a rate of $102 \mu\text{m}/\text{yr}$ in a 0.3% solution. Corrosion rates are accelerated by concentrated solutions, cupric salts, aeration, and elevated temperatures.

8.1.3 Hydrofluoric Acid

Many copper alloys have useful resistance to certain concentrations of hydrofluoric acid. In unaerated, stagnant solutions, aluminum bronze resists all concentrations up to 70%. At the boiling temperature, Cu-30Ni resists all concentrations of hydrofluoric acid, including hot concentrated acid. Aeration or oxidizing agents considerably increase the corrosion rate.

8.1.4 Sulfuric Acid

Quiet submersion of copper in 0.05% sulfuric acid at room temperature corrodes copper at a rate of $76 \mu\text{m}/\text{yr}$. At higher temperatures and concentrations, sulfuric acid acts as an oxidizer and corrodes copper rapidly. Corrosion usually occurs as pits, and the pits are filled with copper sulfide. Oxygen is not necessary for this action but promotes it. Aeration and elevated temperature generally increase corrosion rates. For purposes of comparison, copper and Cu-30Ni corrosion rates in 10% acid solution at 60°C are 483 and $305 \mu\text{m}/\text{yr}$, respectively.

8.1.5 Sulfurous Acid

The high copper alloys at ordinary temperatures are corroded at rates of about 127 to $381 \mu\text{m}/\text{yr}$. No acid concentration was given.

8.1.6 Phosphoric Acid

In quiet immersion at 42% acid solution at 16°C , copper corrodes at a rate of $406 \mu\text{m}/\text{yr}$. Aeration accelerates the rate, but elevated temperatures decelerate it. Aluminum bronzes have similar corrosion rates. Oxidizing agents, such as ferric salts, enhance the corrosion rates.

8.2 Alkaline Solutions

8.2.1 Caustic Alkalies

Copper and its alloys are only slowly corroded by caustic alkalies (sodium hydroxide and potassium hydroxide). For quiet immersion in 3.9% NaOH at 30°C , copper corrodes at $360 \mu\text{m}/\text{yr}$. For the alloys, corrosion rates might vary from 5 to $50 \mu\text{m}/\text{yr}$. The cupronickels are the most resistant of the candidate copper alloys to alkali solutions.

8.2.2 Ammonia

Moist ammonia and ammonium hydroxide solutions corrode copper and most of its alloys rapidly in the presence of air because of the formation of soluble copper compounds. For quiet immersion in 3.5% ammonium hydroxide at room temperature, copper corrodes at 650 $\mu\text{m}/\text{yr}$. It is interesting that 1 ppm of ammonia in nondegassed distilled water gave a pH of 7.7 and prevented the pickup of copper by the water. The cupronickels are the most resistant of the candidates to ammonium hydroxide and are also the most resistant to stress corrosion cracking.

8.3 Neutral Solutions

8.3.1 Salt Solutions

Copper and its alloys have good resistance to many salt solutions, such as the sulfates and nitrates of sodium, potassium, magnesium, and calcium. Corrosion rates are about 5 $\mu\text{m}/\text{yr}$ under quiescent conditions and somewhat higher under aerated and agitated conditions. Chlorides are usually more corrosive, primarily because of the formation of metal-ion concentration cells. Corrosion rates range from 15 to 280 $\mu\text{m}/\text{yr}$. Aeration and agitation strongly enhance the chloride attack.

The alkaline salts (carbonates, silicates, and phosphates) produce a slightly higher rate of corrosion than do the sulfates and nitrates. The chromates do not corrode copper in neutral or alkaline solutions, but do corrode copper strongly in acid solutions.

Cyanide solutions are corrosive because of the formation of soluble copper cyanide salts. Hypochlorites corrode copper alloys by localized pitting and at rates greater than 508 $\mu\text{m}/\text{yr}$.

Ammonium salts are corrosive to copper alloys, particularly when the solution is aerated. The most resistant of the candidate copper alloys is cupronickel (Cu-30Ni). The corrosion rate of copper ranges from 50 to 330 $\mu\text{m}/\text{yr}$.

Oxidizing acid salt solutions of ferric, cupric, mercuric, stannic, and silver salts are strongly

corrosive to copper alloys. The chloride salts are particularly corrosive. Mercury salt solutions will also cause rapid cracking of many copper alloys under tensile stresses, either residual stresses from cold working or applied stresses. Nonoxidizing acid salts (such as aluminum chloride) are moderately corrosive in unaerated solutions but become more aggressive in aerated and agitated solutions.

8.3.2 Fresh Water

Copper and its alloys react very similarly in fresh water. Corrosion rates are generally about 5 to 25 $\mu\text{m}/\text{yr}$ and often less. Protective films of lime (CaOH) compounds form on copper in hard water, so these waters are seldom corrosive. Soft waters containing free carbon dioxide can be corrosive to copper. Tests conducted at room temperature for 24 hr in water saturated with air and carbon dioxide gave corrosion rates of 50 and 150 $\mu\text{m}/\text{yr}$, respectively.

8.3.3 Salt Water

Copper alloys offer good resistance to corrosion in seawater, partly because of the formation of protective overlayers of corrosion products and partly because of the inherent nobility of the high-copper alloys. Corrosion rates of copper alloys in seawater depend on the concentration of salts in the seawater, the temperature, the water velocity, and the degree and kind of pollution if present. The composition of the alloy is of primary importance in corrosion resistance.

The corrosion rates of copper alloys in clean, quiescent seawater range from 5 to 50 $\mu\text{m}/\text{yr}$. The rates increase substantially when the effects of velocity and water pollution are involved. Turbulent flow and high velocity of seawater can prevent or remove protective films so as to permit local and rapid corrosion (corrosion erosion). Of the candidate materials, the Cu-30Ni performs best in seawater, followed by aluminum bronze (5% aluminum), and then pure copper. The iron in cupronickel results in the formation of better protective films in seawaters than those formed on cupronickel alloys without iron.

9. Archaeological Metallurgy

The slow rates of atmospheric corrosion of copper and its alloys are indicated by the wide use of copper as an architectural material. For example, the use of copper roofs on public buildings in Scandinavia dates back to the 13th century [105]. The composition of the corrosion layer on copper roofs in the United Kingdom has been extensively studied [106]. These roofs, some of which are believed to be at least 300 yr old, have been characterized as a function of the type of atmosphere to which they were exposed. The patina formed in rural atmospheres has copper salts of sulfate and carbonate; in urban or industrial atmospheres, sulfate, carbonate, and chloride salts; in marine atmospheres, chloride, carbonate, and sulfate salts; and in mixed urban-marine atmospheres, sulfate, carbonate, and chloride salts.

The Statue of Liberty in New York Harbor is another example of the archaeological metallurgy of copper [91]. The statue is over 100 yr old and has been subjected to a polluted marine environment. Corrosion rates vary from 1.6 to $0.8 \mu\text{m/yr}$, depending on location and composition (the statue is generally 95 to 98% copper with significant amounts of zinc). The characterization

of the corrosion of the statue was discussed in more detail in Sec. 6.2.

Cannons recovered from a sunken Swedish warship, the Kronan, also indicate the lack of reactivity of copper [107]. These cannons were underwater for more than three centuries (1676–1980), some completely buried in the clay of the Baltic seafloor. According to the author, "most of the cannons showed no deterioration—once cleaned they look almost as new and perfect as they did on the day they were cast." The recovered cannons were primarily copper-tin alloys, except for one that was of high copper content (98.5%).

Evidence of the use of copper-nickel alloys dates back thousands of years [108]. The earliest copper-nickel alloy objects that are known to have survived to the present day are coins minted in Bactria, an ancient kingdom situated north of present-day Afghanistan [109]. The coins (ca. 200–190 BC) were issued during the reign of the Greek king Euthydemus II and contain 20.038% nickel and 77.585% copper [110]. This is very near to the concentration of CDA 613.

10. Ranking of the Copper-Based Candidate Alloys

Considering only the effects of oxidation and corrosion on the copper-based candidate alloys, the following ranking is proposed:

1. CDA 715 and CDA 613
2. CDA 102

The cupronickel alloy (CDA 715) and the aluminum bronze alloy (CDA 613) are ranked together since they behave similarly in all of the

environments reviewed (dry-air, atmospheric, and aqueous). A clear distinction could not be made between the two alloys in terms of corrosion performance. The pure copper alloy (CDA 102) has the lowest general corrosion resistance in all of the environments reviewed and is also the alloy most susceptible to localized corrosion (pitting) in seawater.

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12. References

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