

Report on the Corrosion of Certain Alloys

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Table of Contents

	Executive Summary	3
I.	Introduction	4
II.	Definitions for Alloys and Corrosion	5
III.	Atmospheric Environments	7
IV.	Soil and Groundwater Environments	8
V.	Seawater or Marine Environments	10
VI.	Types of Stainless Steels	12
VII.	General Corrosion of Stainless Steels	18
VIII.	Microbiologically Induced Corrosion (MIC)	28
IX.	Copper and Copper Alloys	31
X.	Specific Properties of Copper Wrought Alloys	34
XI.	Specific Properties of Cast Copper Alloys	37
XII.	General Corrosion of Copper Alloys, i.e., Brass and Bronze	42
XIII.	Bench-Scale Study to Determine the Corrosivity/Leachability of Various Metals from Metal Alloys	50
XIV.	Corrosion and Availability of Chromium, Nickel, and Copper	53
XV.	General Summary of Peer Reviewers Comments	63
XVI.	Conclusions	64
XVII.	References	66

Executive Summary

In the early 1990s, EPA received several petitions to delist chromium, nickel, and copper when found in stainless steel, brass, and bronze (alloys that contain chromium, nickel, and copper) from the EPCRA section 313 list of toxic substances. The underlying basis of these petitions was that the petitioners believe that these metals, as they exist in these alloys, are not available and will not become available, to exert their toxicity when released to the environment. These petitions were denied based on the Agency's determinations that: (1) chromium, copper, and nickel meet the criteria of EPCRA section 313(d)(2)(B) and (C); and (2) corrosion of certain forms (e.g., dusts, grindings, and shavings) of the alloys brass, bronze, and stainless steel can reasonably be anticipated to occur under some processing, use, or disposal situations yielding soluble forms of these constituent metals. The petitioners failed to provide, nor did the EPA possess any data to support the petitioners' contention that manufacturing, processing, use, or other activities involving the metal alloys would not lead to availability of these metals.

In the notice denying these petitions EPA solicited public comment on the reporting of chromium, nickel, and copper in stainless steel, brass, and bronze alloys. EPA specifically requested comment on whether the reporting of chromium, copper, and nickel in certain forms (e.g., blocks) of the alloys should be exempted from the reporting requirements of EPCRA section 313. EPA stated that depending upon the nature of the information submitted, EPA would consider proposing a qualification to the EPCRA section 313 listing to exempt from reporting those forms of an alloy for which data can be provided that indicate corrosion will not occur. In the comments received EPA did not receive sufficient information to propose any such qualifier. However, EPA has continued to review this issue to determine if an exemption qualifier for alloys is scientifically supportable. To this end the Agency directed a comprehensive review and analysis of available data pertaining largely to the stability and fate of stainless steel, brass, and bronze alloys in the environment, the availability of their constituent metals, and prepare a report that describes the results of this undertaking. The Agency had the report peer reviewed, and revised the report accordingly. The present document is the revised version of the report.

I. Introduction

Petitions were received by the EPA on June 12, 1992 from Russell Harrington Cutlery, Inc., on September 25, 1992 from Bath Iron Works Corporation, and on October 1, 1992 from Stillwater Fasteners, Inc. to delist chromium, nickel, and copper when found in stainless steel, brass, and bronze alloys. These petitions were denied on June 29, 1993 based on the Agency's determinations that: (1) chromium, copper, and nickel meet the listing criteria of EPCRA section 313(d)(2)(B) and (C); and (2) corrosion of certain forms (e.g., dusts, grindings, and shavings) of the stainless steel, brass, and bronze alloys and can be reasonably be anticipated to occur under some processing, use, or disposal situations yielding soluble forms of the constituent metals. The petitioners failed to provide, nor did the EPA possess any data to support the petitioners' contention that manufacturing, processing, use, or other activities involving the metal alloys would not lead to availability of the constituent metals.⁽¹⁾ After the petition denial was published in the Federal Register a letter was received by the EPA on October 15, 1993 from Independent Nail Company again requesting that EPA delist chromium, nickel, and copper when found in stainless steel, brass, and bronze alloys.

In the 1993 denial notice EPA requested comments on the reporting of chromium, nickel, and copper in stainless steel, brass, and bronze alloys. EPA specifically requested comment on whether the reporting of chromium, copper, and nickel in certain forms (e.g., blocks) of the alloys should be exempted from the reporting requirements of EPCRA section 313. EPA stated that depending upon the nature of the information submitted, EPA would consider proposing a qualification to the EPCRA section 313 listing to exempt from reporting those forms of an alloy for which data can be provided that indicate corrosion will not occur. In the comments received, EPA did not receive sufficient information to propose any such qualifier. However, EPA has continued to review this issue to determine if an exemption qualifier for alloys is scientifically supportable. To this end the Agency directed the Syracuse Research Corporation to perform a comprehensive review and analysis of available data pertaining largely to the stability and fate of stainless steel, brass and bronze alloys in the environment, the availability of their constituent metals, and prepare a document that describes the results of this undertaking.⁽²⁾ The present document has been developed from the information that has been obtained from this review.

To identify and locate information on the stability (i.e., environmental fate, corrosion) of stainless steels, brass, and bronze alloys in the environment, organizations, such as NACE (National Association of Corrosion Engineers) International, were contacted to see whether they knew of any research and experts in the area of environmental fate/corrosion of alloys. Their list of publications was also reviewed for any useful references.

The world-wide web was used to visit sites of organizations, journals, companies, and universities to locate material on fate/corrosion. The web was also used to locate fate/corrosion discussion groups which were joined. A request for sources of information or contacts relevant to

fate/corrosion of alloys was also posted on the web.

Books and research papers that may contain information on corrosion of alloys were identified, obtained, and reviewed. Tables of contents of books that are compendia or collections of articles or reviews were reviewed for purposes of identifying useful information on corrosion of stainless steel, brass, and bronze.

The information obtained on corrosion and corrosion studies on stainless steel, brass, and/or bronze alloys is summarized in the following seventeen sections. The terms alloy and corrosion are defined in section II followed by three sections on the major types of environments and how these environments can affect the corrosion resistance of the alloys. Sections VI and VII describe the types of stainless steels followed by a discussion of some of the major corrosion studies that have been done on stainless steels. Section VIII deals with MIC (microbiologically induced corrosion). Sections IX, X, XI, and XII describe the types of copper alloys followed by a discussion of some of the major corrosion studies that have been done on copper alloys. Section XIII discusses the bench scale study done by the Dragun Corporation for the AAMA (American Automobile Manufacturers Association) in response to a request by the EPA for additional leachability and corrosion studies on stainless steels and copper alloys. This is followed by a section on how the environment can affect the availability of chromium, nickel, and copper. Section XV is a general summary of comments by peer reviewers followed by the conclusions and references in sections XVI and XVII.

II. Definitions of Alloy and Corrosion

The definition of “alloy” is: an intentional mixing of two or more chemical elements that have at least one metallic property; examples being stainless steel, brass, and bronze, which are three of the most commonly used alloys.⁽³⁾ The major metal in stainless steel is iron; however, depending on the type of stainless steel there can be substantial amounts of chromium and/or nickel, which are added to minimize the corrosion of the stainless steel. The major metal in brass and bronze is copper; however, substantial amounts of nickel and/or zinc may also be present. Brass is an alloy of copper and zinc with other metals in varying lesser amounts. Bronze is an alloy of copper and tin with traces of other metals.

All metals and alloys undergo corrosion, which is defined as the destructive attack of a metal by the environment, by chemicals, or electrochemical processes. The driving force is the free energy of reaction of the metal to form a metal oxide (generally). Since corrosion reactions generally occur on the metal surface, they are called interfacial processes. The corrosion process takes place at the metal-medium phase boundary and therefore is a heterogeneous reaction in which the structure and condition of the metal surface have a significant role (e.g., whether the surface is uncoated, coated with an adhesive, compact, or loose porous coating, or whether its properties have been changed by machining and processing). The corrosive medium must be transported to the surface and the corrosion products removed. Therefore, material transport phenomena, including free convection and diffusion into adjacent surface layers, must also be taken into account.⁽⁴⁾ Some metals, like sodium, undergo

“corrosion” within minutes while other metals, like gold and mercury, undergo “corrosion” only after years of exposure. The same is true with alloys; some alloys undergo corrosion within days (e.g., low carbon steel and some types of stainless steel) while other alloys (e.g., copper/nickel/zinc alloy) are relatively resistant and undergo corrosion only after years of exposure.

Metallurgical factors that can affect corrosion in an alloy include: crystallography, grain size and shape, grain heterogeneity, impurity inclusions, and residual stress due to cold work. In stainless steel, sensitization is the most important metallurgical factor affecting corrosion resistance. Sensitization is the precipitation of chromium carbides in grain boundaries giving rise to chromium depletion. It applies only to austenitic grades and the consequent intergranular corrosion is observed primarily in chemical environments. It is rarely observed in water or soils of < 3000 ppm chloride. In copper alloys, residual stress left from forming may cause stress corrosion cracking. Brass is subject to dezincification.⁽⁵⁾

There are eight forms of corrosion (based on visual characteristics)⁽⁶⁾. These are:

- 1) Uniform corrosion: most common form of corrosion, characterized by a chemical-electrochemical reaction over the entire exposed surface;
- 2) Galvanic corrosion or two-metal corrosion: driving force for current flow and metal corrosion is the potential developed between the two metals;
- 3) Crevice corrosion: intense localized corrosion that occurs frequently within crevices on metal surfaces exposed to corrosives;
- 4) Pit corrosion: localized attack that results in holes in the metal. This is one of the most destructive forms of corrosion;
- 5) Intergranular corrosion: localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains. It can be caused by impurities at the grain boundaries causing the alloy to disintegrate and/or lose its strength;
- 6) Selective leaching: removal of one element from a solid alloy by corrosion processes;
- 7) Erosion corrosion: acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface; and
- 8) Stress corrosion: caused by the simultaneous presence of tensile stress and a specific corrosive medium.

Recent studies have expanded the corrosion categories and redefined them by mechanisms rather than by visual appearance. Overlap between the mechanisms may exist. The five general categories include:

- 1) General corrosion;
- 2) Localized corrosion;
- 3) Metallurgically influenced corrosion;
- 4) Mechanically assisted degradation;
- 5) Environmentally induced cracking.

Corrosion can be accelerated by differential temperature cells or by the presence of mechanical forces in conjunction with chemical forces. There are six major factors that affect the rate of corrosion of alloys in an aqueous environment:

- 1) acidity;
- 2) presence or absence of oxidizing agents;
- 3) presence or absence of films on the alloy;
- 4) temperature;
- 5) velocity of moving aqueous solution;
- 6) heterogeneity both in the solution and in the alloy.

Any one or a combination of these factors may control the rate of corrosion of the alloy in any given circumstance.⁽⁷⁾

III. Atmospheric Environments

Specific factors influencing the corrosivity of atmospheres are dust content, gases in the atmosphere, and moisture (critical humidity). Atmospheres are often classified as rural, industrial, or marine in nature, but this is an over simplification. There are locations along the seacoast that have heavy industrial pollution in the atmosphere and so are both marine and industrial. Two decidedly rural environments can differ widely in average yearly rainfall and temperature and therefore can have considerably different corrosive tendencies. Industrial expansion into formerly rural areas can easily change the aggressiveness of a particular location. Finally, long-term trends in the environment, such as changes in rainfall pattern, mean temperature, and acidity of the rainfall, can make extrapolations from past behavior much less reliable. Other factors that limit the usefulness of atmospheric exposure data are the general nonlinearity of weight loss due to corrosion over time and the fact that most atmospheric corrosion data are presented as an average over the entire test panel surface. Most atmospheric exposure data for steels show a decrease in the rate of attack with duration of exposure so that extrapolations of such data to times longer than those covered by the exposure data can lead to significant errors.⁽⁸⁾

Atmospheric corrosion proceeds in a relatively complicated system consisting of surface electrolyte, atmosphere, metal, and corrosion products. Analyses of the corrosion products give the following general characteristics. Nearly all nitrates and acetates are soluble and these anions are not

found in corrosion films. An exception to this is with copper where basic nitrates have been detected. Simple chlorides and sulfates are soluble and generally are not found in corrosion films. All hydroxides are insoluble as are many mixed salts that include hydroxide as one of the constituents. Both hydroxides and mixed salts are common corrosion products. Normal and hydroxy carbonates are common constituents of corrosion films. Atmospheric corrosion is an electrochemical process with the electrolyte being a thin layer of moisture on the metal surface. The composition of the electrolyte depends primarily on the deposition rates of the air pollutants and varies with the wetting conditions. Environmental factors can cause the median thickness loss to vary by as much as 50% or more in a few extreme cases. Those environmental factors that tend to accelerate metal loss include high humidity, high temperature (either ambient or due to solar radiation), proximity to the ocean, extended periods of wetness, and the presence of pollutants in the atmosphere, such as sulfur oxides (SO_x), nitrogen oxides (NO_x), hydrogen sulfide, ammonia, and carbonyl sulfide (COS). The most important corrosive constituent of industrial atmospheres is sulfur dioxide, which originates predominately from the burning of coal, oil, and gasoline. The small amount of carbon dioxide normally present in the air, neither initiates nor accelerates corrosion.^(9,10)

Metallurgical factors can also affect metal loss. Within a given alloy family, those with a higher alloy content tend to corrode at a lower rate. Surface finish also plays a role in that a highly polished metal will corrode slower than one with a rougher surface.⁽¹¹⁾

The atmospheric contaminants most often responsible for the rusting of structural stainless steels are chlorides and metallic iron dust. Chloride contamination may originate from the calcium chloride used to make concrete, from exposure in marine or industrial locations, or from the use of road salts. Rural atmospheres, uncontaminated by industrial fumes or coastal salt, are extremely mild in terms of corrosivity for stainless steel, even in areas of high humidity. Industrial or marine environments can be considerably more severe.⁽¹²⁾

Copper and copper alloys are suitable for atmospheric exposure. They resist corrosion by industrial, marine, and rural atmospheres, except atmospheres containing ammonia, sulfur dioxide, or oxides of nitrogen. The severity of the corrosion attack in marine atmospheres is somewhat less than that in industrial atmospheres, but greater than that in rural atmospheres. However, these rates decrease with time due mainly to the formation of a protective film (e.g., copper chloride or copper sulfate) that develops on the surface of the copper or copper alloy.

IV. Soil and Groundwater Environments

Soils are defined as unconsolidated rock material over bedrock and/or freely divided rock-derived material containing a mixture of organic matter and capable of supporting vegetation. Worldwide, corrosion of metals in soil is responsible for a large percentage of corrosion and corrosion failures. While several individual characteristics of soils have been used to indicate the corrosivity of

soils, currently no method describes the synergistic effects of these characteristics. In particular, the corrosivity of soil is based largely upon the interaction of electrical resistivity, dissolved salts, moisture content, total acidity, bacterial activity, and concentration of oxygen. Other secondary factors are also important but are more difficult to define. Thus, simply testing metals and alloys in a variable pH solution or in aerated or deaerated solutions will not accurately describe the conditions in soil.⁽¹³⁾ In addition, soil environments are generally stationary electrolyte exposure conditions. Therefore, depleting and/or concentrating effects can occur at the surface of alloys.

However, some factors associated with the soil environment which can have an impact on the corrosion rates of metal alloys include: soil texture, internal drainage, resistivity, redox potential, moisture content, permeability, chloride ion content, sulfide and sulfate ion content, presence of corrosion-activating bacteria, oxygen content, pH, total hardness and hardness as calcium carbonate of soil moisture, and stray direct currents (dc).^(14,15,16)

Soil texture is determined by the proportions of sand, silt, and clay that make up a soil. Clay, having the finest particle size and minimum pore volume between particles, tends to reduce the movement of air and water and can develop conditions of poor aeration when wet. Sand has the largest particle size and promotes increased aeration and distribution of moisture. Soil texture thus has as important influence on the diffusivity of soluble salts and gases.

Internal drainage is that property of soil that describes the water retention properties of a soil and is related to soil texture. Internal drainage is also affected by the height of the water table. Thus, a sandy soil which would normally have good permeation to moisture is considered to have poor internal drainage if the water table is high and keeps the soil in a saturated condition.

Soil resistivity is a measure of how easily a soil will allow an electric current to flow through it. This is also a measure of how effective the soil is as an electrolyte. The lower the resistivity of a soil, the better it will behave as an electrolyte and the more likely it is to promote corrosion. A soil with a resistivity below 500 ohm-cm is considered to be corrosive. Above 2000 ohm-cm the relation of soil resistivity to soil corrosivity is less reliable.

The temperature of the soil is an important factor in the corrosion process. The resistivity of soil is inversely proportional to temperature and therefore an increase in soil temperature would be expected to increase the rate of the corrosion reaction. However, an increase in temperature also reduces the solubility of oxygen, which tends to reduce the rate of reaction. The net result is that soil temperature does not have as large an effect on underground corrosion as would be expected.

Soil pH is the acidity or alkalinity of the soil media. Most soils and all loams are fairly well buffered, resulting in a soil pH that is not affected by rainfall. Sand, because of its high moisture diffusivity, can have its soluble salts leached out or diluted to the point that its pH will change during a heavy rain. This can cause the corrosion rate to either increase or decrease.

The redox potential or oxidation-reduction potential of a soil gives an indication of the proportions of oxidized and reduced species in that soil. Very high corrosion rates can occur in poorly aerated (reducing) soils where anaerobic bacteria often thrive.

The presence of increasing concentrations of chloride ions lowers the resistivity of soil and water and will cause an increase in the corrosion rate. The presence of sulfides and sulfates is often an indicator of sulfate reducing bacteria (SRB's). These bacteria can shift the pH in the acidic direction, causing an increase in corrosion. The higher the water hardness, i.e., the higher the concentration of calcium carbonate in the soil, the lower the corrosion rate will be.

Another kind of corrosion that has become more important, particularly in large cities, is stray current corrosion. Stray electric currents are those that follow paths other than the intended circuit, or they may be any extraneous currents in the earth. Stray current corrosion is one of the most destructive kinds of corrosion in large cities where exposure to underground lines, electric trains, etc. is significant. Sources of direct stray currents are commonly electric railways, grounded electric dc power lines, electric welding machines, cathodic protection systems, and electroplating plants. Sources of stray alternating current (ac) are usually grounded ac power lines or currents induced in lines.⁽¹⁷⁾

Naturally occurring waters are seldom pure. Even rainwater, contains oxygen, nitrogen, carbon dioxide, and other gases, as well as entrained dust and smoke particles. Water that runs over the ground carries eroded soil, decaying vegetation, living microorganisms, dissolved salts, and colloidal and suspended matter with it. Water that seeps through soil contains dissolved carbon dioxide and becomes acidic. Groundwater also contains salts of calcium, magnesium, iron, and manganese. All these foreign substances in natural water affect the structure and composition of the resulting films and corrosion products on the surface of metals and alloys, which in turn control the corrosion of the metal or alloy involved. Permanganate ion, which is associated with the dumping of chemicals, has been shown to cause corrosion of stainless steels. Reduction products of potassium permanganate and manganese salts discharged from steel mills can cause under deposit corrosion or microbiologically induced corrosion. In addition to these substances, the aqueous corrosion of the metal or alloy can be influenced by such factors as pH, time of exposure, temperature, motion, and fluid agitation.⁽¹⁸⁾

V. Seawater or Marine Environments

Seawater is a biologically active medium that contains a large number of microscopic and macroscopic organisms. Many of these organisms are commonly observed in association with solid surfaces in seawater, where they form biofouling films. Immersion of any solid surface in seawater initiates a continuous and dynamic process, beginning with adsorption of nonliving, dissolved organic material and continuing through the formation of bacterial and algae slime films and the settlement and growth of various macroscopic plants and animals. This process, by which the surfaces of all structural

materials immersed in seawater become colonized, adds to the variability of the ocean environment in which corrosion occurs.

The amount of oxygen and other gases dissolved in seawater depends on the temperature and the salinity of the seawater and the depth. In some seawater compositions, hydrogen sulfide is also present. Hydrogen sulfide is formed in seawater by the action of sulfate-reducing bacteria (SRB), usually under deposits where oxygen is depleted or when the seawater is stagnant or polluted and becomes anaerobic, even in large volumes. Silt deposits in estuarial waters are also contributory. Mineral and organic materials are also carried in suspension by the seawater, particularly near the mouths of rivers.⁽¹⁹⁾

Since seawater is a complex, delicately balanced solution of many salts containing living matter, suspended silt, dissolved gases, and decaying organic material, the individual effect of each of the factors affecting the corrosion behavior is not readily separated. Because of the interrelation between many of the variables in the seawater environment, an alteration in one variable may affect the relative magnitude of the other variables. The factors which effect the amount or rate of corrosion may be divided into chemical, physical, and biological. The roles of oxygen, biological activity, temperature, velocity, salinity, and pH are discussed below.^(20,21)

Oxygen

The dissolved oxygen content is a major factor affecting the corrosivity of seawater. The oxygen level in seawater many range up to 12 ppm. Photosynthesis of green plants, wave action, etc., tend to increase the oxygen level, whereas the biological oxygen demand of decomposing dead organisms will reduce it. For a given location, seasonal variation in oxygen level will influence corrosion behavior. For metals like copper and iron, complete elimination of oxygen will reduce the corrosion to negligible amounts. However, metals that depend on formation of a passive film for corrosion protection, e.g., stainless steels, often corrode rapidly where the oxygen supply to the metal surface is restricted.

Biological Activity

When a metal or other surface is first immersed in seawater, a biological slime tends to develop in a matter of hours. During an active season, a great variety of organisms are found on an immersed surface. From a corrosion point of view, the sessile organisms are of most concern. They arrive at the slime-covered surfaces in minute embryonic form and become firmly attached. Once attached, they rapidly transform to the mature form and become immobile. Organisms which build hard shells are: annelids, barnacles, encrusting Bryozoa, mollusks, and corals. Organisms without hard shells are: marine algae, filamentous Bryozoa, coelenterates or hydroids, tunicates, and calcareous and silaceous sponges.

Temperature

An increase in temperature is normally expected to speed up a chemical reaction according to

thermodynamic considerations. This also would be the case for the corrosion reaction in seawater were it possible to hold all other variables fixed. Since it is not normally possible to do this, the effect of temperature has to be established indirectly. Oxygen solubility decreases with increase in temperature, biological activity increases as the water temperature increases, and the chemical equilibrium involved in the precipitation of calcium carbonate and magnesium hydroxide is altered so that calcareous scale is more likely to deposit on the metal as the temperature is increased. For temperature variations of a seasonal nature, iron, copper, and many of their alloys show a high rate of attack during the warm months.

Velocity

Many metals are sensitive to velocity effects in seawater. For metals like iron or copper, there is a critical velocity beyond which corrosion becomes excessive. Stainless steel and certain nickel-chrome-molybdenum alloys tend to be more resistant in high-velocity seawater. Special forms of corrosion are associated with seawater velocity, e.g., (1) erosion-corrosion caused by high-velocity silt-bearing seawater, (2) impingement attack, where air bubbles are present, and (3) cavitation, where collapsing vapor bubbles cause mechanical damage and often corrosion damage as well.

Salinity

The major oceans of the world are completely connected and mixing is continuous. The average salt content of the sea is 3.5 wt% with the composition comprised mainly of the following ions: sodium, magnesium, calcium, potassium, chloride, bromide, carbonate, and sulfate. In addition, seawater contains measurable quantities of iodide, fluoride, phosphate, gold, silver, arsenic, rubidium, copper, barium, manganese, lithium, lead, iron, strontium, and zinc ions. Ammonia is also present, with free oxygen, nitrogen, and other gases. Variations in salinity in open-ocean surface water typically range from 3.25 - 3.75 wt%.

pH

The pH of seawater may vary slightly depending on the photosynthetic activity. Plant matter consumes carbon dioxide and affects the pH during the daylight hours. The carbon dioxide content in seawater is influenced, close to the surface, by the exchange with carbon dioxide in the atmosphere. The slight daily shift in pH has little direct effect on the corrosion behavior, however, it can be a factor in calcareous-scale deposition, which affects the corrosivity. As pressure is increased, pH is reduced according to thermodynamic considerations. Thus, at great depths, there is some evidence of less tendency for protective carbonate-type scale formation.

VI. Types of Stainless Steels

The American Iron and Steel Institute (AISI) defines alloy steels as follows: "by common custom steel is considered to be alloy steel when the maximum of the range given for the content of

alloying elements exceeds one or more of the following limits: manganese (Mn), 1.65%; silicon (Si), 0.60%; copper (Cu), 0.60%; or in which a definite range or a definite minimum quantity of any of the following elements is specified or required within the limits of the recognized field of constructional alloy steels: aluminum (Al), boron (B), chromium (Cr) up to 4.00%, cobalt (Co), niobium (Nb), molybdenum (Mo), nickel (Ni), titanium (Ti), tungsten (W), vanadium (V), zirconium (Zr), or any other alloying element added to obtain a desired alloying effect.”

More than 180 different alloys belong to the stainless steel group and each year new ones and modifications of existing ones appear. In some stainless steels the chromium content now approaches 30%. The major characteristics of stainless steels, containing at least 11% chromium, are corrosion and oxidation resistance, which increase as the chromium content is increased. The main reason for the existence of stainless steels is their resistance to corrosion. By increasing the amount of the chromium content and by the presence of other elements, such as molybdenum or titanium, the corrosion resistance of stainless steels can be varied over a tremendous range. Steels that contain 4.00% or more of chromium are included, by convention, among the special types of alloy steels known as stainless steels.⁽²²⁾ However, the high chromium heat resistant steels (5% chromium, 5% molybdenum) are not true stainless steels. An inherent truly passive film, which occurs on stainless steels, only develops when the chromium content is above about 11%. The corrosion performance of stainless steels can also be strongly affected by practices of design, fabrication, surface conditioning, and maintenance.

Stainless steels produced in the United States can be identified in three general ways: (1) by the Unified Numbering System (UNS) numbers developed by the American Society for Testing and Materials (ASTM) and the Society of Automotive Engineers (SAE) for all commercial metals and alloys; (2) by the American Iron and Steel Institute (AISI) numbering system; and (3) by the names based on compositional abbreviations, proprietary designations, and trademarks. The UNS number comprises six symbols (i.e., a letter followed by five numbers) that are difficult to recognize instantly and memorize for the 180 stainless steels. Therefore, technical journals allow each alloy to be initially identified by the lengthy UNS number and then subsequently the better-known AISI or another designation may be used. The AISI number designates the wrought standard grades of stainless steels by three-digit numbers. Three groups of wrought stainless steels, series 200, 300, and 400, have composition limits standardized by the AISI. Steels in the AISI 400 series contain a minimum of 11.5% chromium and usually not more than 2.5% of any other alloying element. Steels in the AISI 300 series contain a minimum of 16% chromium and 6% nickel; the relative amounts of these elements are balanced to give an austenitic structure. Austenitic structures have face-centered cubic lattices, while ferritic structures have body-centered cubic lattices and martensitic structures have body-centered tetragonal or cubic lattices. Stainless steels containing both austenite and ferrite, usually in roughly equal amounts, are known as duplex. Duplex stainless steels, precipitation-hardening stainless steels, and higher alloys containing less than 50% iron (Fe) do not have AISI designations and are generally known by names based on compositional abbreviations and trademarks, as well as UNS numbers.^(23,24)

The many grades of stainless steel are due to the crystal structure of the iron-rich matrix. The

austenite field in iron exists over an increasingly small temperature range as chromium is added, and disappears at about 12% chromium. To make the martensitic grades, it is important to be able to form 100% austenite first. Fortunately carbon extends the austenite range so it is possible to have all austenite prior to quenching in a 12% chromium carbon steel, or if the carbon content is high enough, even in a 17% chromium steel. Adding several percent of nickel to an iron-chromium alloy can allow austenite to exist as metastable or stable forms down to ambient temperature. A body-centered cubic phase, or sometimes a hexagonal close-packed phase, can then form martensitically, and can give very high strengths to the stainless steel. For the ferrite grades, it is necessary to have at least 12% chromium and only very small amounts of elements that stabilize austenite. For these materials, the structure is body-centered cubic from room temperature to the melting point. Some elements, such as molybdenum, niobium, titanium, and aluminum, which encourage the body-centered cubic structure, may also be in these steels. Compositions of some stainless steels are listed in Table 1.⁽²⁵⁾

Table 1. Typical Composition of some Stainless Steels, wt%

(Sulfur (S) and Phosphorus (P) are held below 0.03 and 0.04% max, respectively, balance is Fe)

AISI #	C	Mn	Si	Cr	Ni	Mo	N	Ti	Nb
201	0.15	6.50	0.75	17.0	4.50		0.20		
202	0.15	8.75	0.75	18.0	5.00		0.20		
205	0.12	15.0	0.50	17.0	1.75		0.35		
304	0.06	1.50	0.75	19.0	10.0				
309	0.16	1.50	0.75	23.0	13.5				
310	0.20	1.50	1.00	25.0	20.5				
316	0.06	1.50	0.75	17.0	12.0	2.50			
321	0.06	1.50	0.75	18.0	10.5			0.50	
330	0.08	2.00	1.00	18.0	35.0				
347	0.06	1.50	0.75	18.0	11.0				1.00
410	0.12	0.75	0.75	12.5					
430	0.10	0.75	0.50	16.0	0.30				
446	0.30	1.00	0.75	25.0			0.20		

There are four major classes of stainless steels. These are:

1) *Austenitic stainless steels*, these are essentially non-magnetic and cannot be hardened by heat treatment. They are hardenable only by cold-working. As a group, these stainless steels have greater corrosion resistance than the other three groups. At the same time there is a wide range in the corrosion resistance among the austenitic types. Most of these steels contain nickel as the principal austenite former, and some contain substantial amounts, 2-4%, of manganese and less nickel. These steels possess better corrosion resistance than the straight chromium steels. Chromium content is generally between 16-26%, with the nickel content generally between 4-22%. The 300 series represents by far the largest category of stainless steels produced in the United States. For the sake of discussion, the austenitic alloys can be divided into four subclasses.^(26,27)

Class A: AISI types 301, 302, 303, 304, 304L, 304N, 321, 347, and 348 are all contained within class A. Each of the types in this group can be considered an 18-8 stainless steel (i.e., 18% chromium content and 8% nickel content). Within this class, there is no great difference in the general corrosion resistance of the individual types. Those that have a higher alloy content are slightly more corrosion resistant than those with a lower alloy content. Types 321, 347, and 348 are carbide stabilized with titanium and/or niobium. Although their general corrosion resistance may be no higher than types 302 or 304, they are essentially immune to sensitization and the possible attendant intergranular corrosion under specific conditions.

Class B: Only types 305 and 384 are contained within class B. These have relatively high nickel contents (12.0% and 15.0%) nominally and respectively. While they both have greater corrosion resistance than the 18-8 steels, they were principally designed for extra-deep drawing and cold heading operations, as allowed by the higher nickel content

Class C: AISI types 302B, 308, 309, 309S, 310, 310S, and 314 are examples of the class C group. Type 302B is a modified 18-8 and has a silicon addition (2.5%) that increases oxidation resistance at elevated temperatures. Type 314 represents a higher alloy version (25% chromium-20% nickel) of an 18-8 steel. It has a silicon addition that is more corrosion resistant, especially to sulfuric acid, than type 302B and also has a high resistance to scaling at elevated temperatures. Types 308, 309, 309S, 310, and 310S are all higher in chromium and nickel and are commonly called 20-11 (20% chromium-11% nickel, type 308), 24-12 (24% chromium-12% nickel, types 309 and 309S) and 25-20 (25% chromium-20% nickel, types 310 and 310S). They have a very high resistance to corrosion and oxidation at elevated temperatures.

Class D: AISI types 316, 316L, 316F, 316N, 317 and 317L are part of this class. They contain at a minimum 16% chromium and at least 2% molybdenum. The ferrite-forming influence of the molybdenum requires an increase in nickel, as an austenite former, to at least 10%. The presence of molybdenum specifically enhances corrosion resistance to chloride pitting and crevice corrosion and also increases general resistance to specific chemicals (e.g., organic acids, amines, phosphoric acid,

dilute sulfuric acid).

2) *Martensitic stainless steels*, these are iron-chromium alloys which are hardened by heat treatment. Heat treatment results in higher strength, with a corresponding proportional diminution of ductility with increasing hardness. Corrosion resistance is less than in the other two groups. In the hardened condition there may be a greater resistance to general corrosion but there is increasingly less resistance to hydrogen-induced cracking. Martensitic steels can be heat-treated to obtain high tensile strengths. The heat treatment results in higher strengths, with a corresponding proportional diminution of ductility with increasing hardness. Corrosion resistance is less than in the other two groups. In the hardened condition, there may be a greater resistance to general corrosion, but there is increasingly less resistance to hydrogen-induced cracking. Chromium content is generally between 11.5-18% with carefully controlled carbon content. Some of the AISI types that make up this group are 403, 410, 414, 416, 420, 420F, 431, 440A, 440B, and 440C.^(28,29)

Types 403, 410, and 416 are known as “turbine quality.” Type 403 is virtually identical to type 410, except that it is made from specially processed and rigorously inspected ingots, as is required for steam turbine blades. Both types contain just enough chromium to maintain “stainlessness” (nominally 12.5%), but there are no significant amounts of other alloying elements. Type 416 is simply 410 with the addition of free-machining additives. Although offering improved machining characteristics, there is a sacrifice in corrosion resistance.

Types 414 and 431 provide better corrosion resistance than type 410, largely because they contain a nominal amount (2.0%) of nickel. These steels have been commonly known as 12-2 (12% chromium-2% nickel) and 16-2 (16% chromium-2% nickel), respectively.

Types 420 and 420F, despite having a higher chromium content than type 410, do not have an appreciably higher corrosion resistance level. Type 420F is almost identical to type 420, except that there is an addition of sulfur to improve machinability. This results in a slight sacrifice of corrosion resistance.

Types 440A, 440B, and 440C are all high-carbon stainless steels and are sometimes called “stainless tool steels.” These types have the highest chromium range of any of the martensitic types, yet their corrosion resistance levels are among the lowest because of their higher carbon content. There is a gradual decrease in corrosion resistance from the A to C subtypes. This is due to the increase in carbon content.

3) *Ferritic stainless steels*, these are nonhardenable steels so designated because they cannot be hardened by heat treatment. They are hardenable only by cold-working. Chromium content is generally between 11.5-27% with low carbon content. Examples of AISI types that make up this group are 405, 409, 429, 430, 430F, 434, 436, 442, and 446. As a group the ferritic stainless steels do not closely approach the austenitic types with respect to corrosion resistance. There are, however,

some ferritic types that may nearly equal the corrosion resistance levels of the austenitics in some environments, but these are exceptions. One of the most interesting aspects of this group of stainless steels is their resistance to stress corrosion.

Type 405, while meeting the minimum requirements for a stainless steel, is actually relatively low in its resistance to corrosion. The carbon level is 0.08% maximum and it has a nominal chromium content of 12.5%. An addition of 0.10 to 0.30% aluminum (a powerful ferritizer) prevents the formation of any appreciable amount of austenite at any temperature. It is thus the ideal grade for welding. Of all the stainless steels, type 409 is generally considered to have the lowest degree of corrosion resistance. It contains very nearly the minimum amount of chromium to qualify as a stainless steel (10.5-11.75%) and is stabilized with titanium.

Types 430, 430F, 434, and 436 represent the old and well-known 17-chrome stainless steel grade, which is the original type 430. Type 430 shows a high resistance against attack by practically all types of atmospheres and also by many types of chemicals, notably oxidizing acids. At times, type 430 replaces the more expensive 18-8 austenitic types. Type 430F is a machinable grade of type 430. The additives contained in it reduce the corrosion resistance of the basic type 430. Type 434 has the same chromium content as type 430, but it has a nominal 1.0% molybdenum content, which adds greatly to its resistance to certain types of corrosion, notably pitting corrosion. Type 436 is essentially type 434, but it contains up to 0.70% niobium plus tantalum for carbide stabilization. Therefore, it is suited for elevated temperature applications as well as for room-temperature corrosion resistance. Types 442 and 446 are frequently called “chrome-irons.” They differ in composition only in chromium content 18.0-20.0% for type 442 and 23.0-27.0% for type 446. Neither is used to any great extent for corrosion resistance at room temperatures. Their principal uses are in heat processing equipment where resistance to scaling is important. Types 442 and 446 are capable of sustained operation at temperatures of 980 °C and 1095 °C respectively, without experiencing destructive scaling. A need for a higher degree of weldability than that provided by type 430 resulted in the development of type 429. Both alloys have the same carbon content; however, 429 has a lower chromium content (14.0-16.0%). This carbon-chromium ratio allows type 429 to retain its ferritic status.^(30,31)

4) The fourth group consists of the *age-hardened or precipitation-hardening steels*. They are hardened and strengthened by solution-quenching followed by heating for substantial times at temperatures in the range of 800-1000 degrees Fahrenheit. Precipitation-hardened stainless steels can have a microstructure consisting of ferrite, martensite, or austenite depending on the heat treatment performed. The precipitation hardening process is thought to involve the formation of very fine intermetallics that impede dislocation motion during deformation, producing higher strength. Prolonged aging cause these intermetallics to coarsen, enabling dislocations to bypass them during deformation, and their strength to begin to decline. In this condition, the material is said to be overaged. AISI types that make up this group include 630, 631, 632, 633, 634, and 660. It is generally considered that the average corrosion resistance of this group approaches that of the 18-8 austenitic grades and that it is usually superior to the corrosion resistance of the martensitic and ferritic types.

Copper is the principal hardening agent in type 630. Its corrosion resistance approaches that of types 302 and 304. In the heat treated condition, type 631 has a duplex structure. Stainless steels that have a duplex structure have a two phase microstructure that exhibits improved strength and high resistance to stress corrosion cracking. With the exception of an addition of molybdenum, type 632 is very much like type 630. There is an improvement in strength and resistance to pitting corrosion due to the addition of molybdenum.

Type 633 is also a duplex-structure grade, but has a slightly higher alloy content than types 631 and 632. Thus, its corrosion resistance is better than types 631 or 632. Type 634 is semiaustenitic (duplex), but it has an alloy content slightly less than type 633. The duplex stainless steels are currently popular for withstanding high chloride environments. These alloys have a two-phase microstructure that exhibits improved strength and high resistance to stress corrosion. Most duplex stainless steels contain high chromium (usually about 25%), low nickel (generally about 8% maximum), and 2-4% molybdenum for enhanced resistance to chloride induced phenomena and to promote general corrosion resistance, specifically pitting corrosion.^(32,33)

The super-austenitic stainless steels include such alloys as 904L and 254MO. These alloys have increased resistance over the austenitic stainless steels due to the addition of 6% molybdenum or other elements.

VII. General Corrosion of Stainless Steels

The mechanism of corrosion resistance for stainless steels differs from that of carbon steels and alloy steels. For the carbon and alloy steels the formation of a barrier of a true oxide separates the metal from the surrounding atmosphere. The degree of protection afforded by the oxide is a function of the thickness of the oxide layer, the continuity of the oxide layer, the coherence and adhesion of the oxide layer to the metal, and the diffusivities of oxygen in the oxide. At normal temperatures stainless steels do not form a layer of a true oxide, instead a passive film is formed. This film is generally considered to be some form of a hydrated oxide. The exact nature of the film is not known, however, it is known that the film must be continuous, nonporous, insoluble, and self-healing if broken in the presence of oxygen. When conditions are favorable for maintaining passivity, stainless steels exhibit very high corrosion resistance. The passive oxide must be free of pores up to the activating potential. Because of the absence of pores for the oxides, it may be concluded that the oxide layer grows directly on the metal. The excellent corrosion protection results because the metal phase can react only negligibly with constituents of the solution, as metal ions or species of the oxidant migrate through the passive film. If passivity is destroyed under conditions that do not permit restoration of the passive film, then stainless steels will corrode much like a carbon or low-alloy steel.⁽³⁴⁾

Corrosion of stainless steels is generally attributed to a breakdown of the passive film at the surface of the material at localized or selective areas. Corrosion may be influenced by one or more of

the following factors:

- 1) inhomogeneities of the metal surface;
- 2) concentration cell effects due to crevices on adhering soil particles where stagnant conditions may exist;
- 3) presence of chloride ion in the soil and/or water;
- 4) abrasion of the metal surface by soil particles or foreign debris and action of water; and
- 5) microbiological organisms present in the soil and/or water.

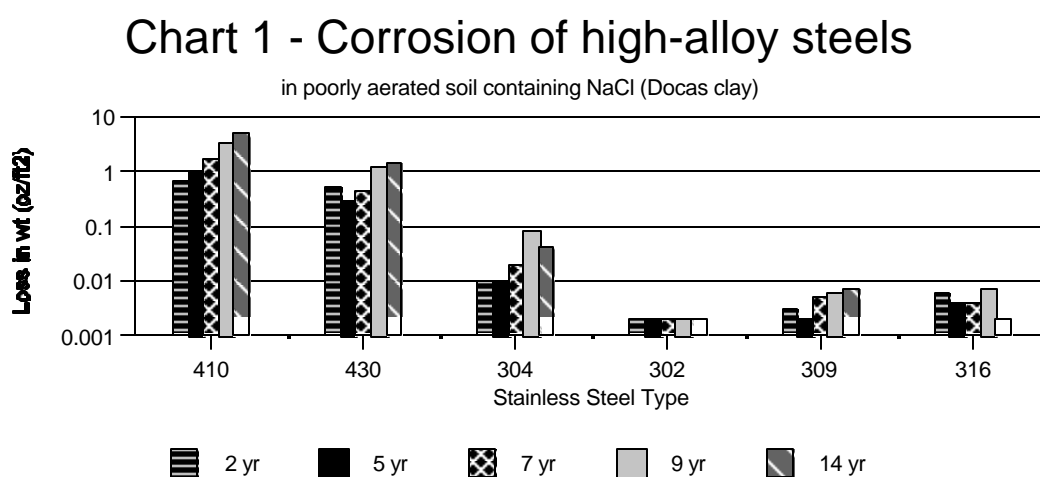
Corrosion is electrochemical in nature and, as such, involves oxidation at a suitable anode and reduction at a suitable cathode. Certain traces of impurities affect the corrosion resistance of metals and alloys. Different faces of a single crystal may have different corrosion rates. The most reactive face on a crystal is a function of the environment in which it is placed with the close packed face generally much more reactive. However, the rate of reaction is a function of the environment, including the influence of dissolved oxygen. The grain boundaries also play an important role in corrosion, frequently functioning as sites for preferential attack either locally or continuously.⁽³⁵⁾ Corrosion rates do not, however, account for corrosion occurring from cracking.

Cathodic protection is defined as the reduction or prevention of corrosion of a metal surface by making it cathodic with the use of sacrificial anodes or impressed current. A number of substances inhibit metallic corrosion by interfering with both anodic and cathodic reactions, thus causing anodic and cathodic polarization.

The corrosion of stainless steels is believed to be a function of the crystallinity, state of hydration, and continuity of films. Environmental conditions influencing these properties control passivity effects and corrosion phenomena.⁽³⁶⁾ In the atmosphere three factors are of fundamental importance: (1) length of time the metal is wet, (2) amount of pollution present in the air, and (3) nature of the corrosion products. If the metal remains dry, its corrosion rate will be low. If the metal becomes wet, the corrosion rate can be appreciable. The specific corrosiveness of a soil is determined by water content of the soil, air content of the soil, and the type of soil as it affects the mobility of the water and the building of protective films.

Corrosion rates can be divided into three categories: linear, decelerating, and accelerating. There are two methods for reporting corrosion rates: thickness of metal corroded per unit area, and weight (gain or loss) per unit area of exposed metal surface per unit time.⁽³⁷⁾ Several studies of the

corrosion behavior of stainless steels in varied environments (soil, marine, air) have been done. One study involved six high-alloy steels placed in poorly aerated soil containing NaCl (Docas clay) for 2, 5, 7, 9, and 14 years, see Chart 1.⁽³⁸⁾ This study reported the corrosion rate in terms of weight loss in oz/ft²; however, there was no mention of the size or the thickness of the specimens that were used. These results show the beneficial effect of nickel in promoting corrosion resistance in stainless steels. Steels that contained from 12 to 18% chromium with only small amounts, less than 0.5%, of nickel, i.e., martensitic stainless steel type 410 and ferritic stainless steel type 430, were found to be much less corrosion resistant than the austenitic stainless steel types 302, 309, and 316 which contain more than 9% nickel.



In fact, types 410 and 430 pitted deeply with perforations or holes occurring within two years, whereas types 302, 309, and 316 showed little or no evidence of corrosion for the maximum period of exposure, fourteen years. There is also corrosion data reported in a National Bureau of Standards (NBS) Circular #579 for the 300 and 400 series of stainless steels buried in various soils for fourteen years that shows essentially the same results, i.e., the 400 series of stainless steels are much less corrosion resistant than the 300 series.⁽³⁹⁾

Another excellent corrosion study involved placing 34 sheet or tube specimens of stainless steels in six different soil types for eight years. The corrosion rate is reported as average weight loss in mg/dm². There was no mention of the size or thickness of the specimens.⁽⁴⁰⁾ See Charts 2a, 2b, and 2c for summaries.

Chart 2a - Corrosion of Stainless Steel

in 6 different soil types for 8 years

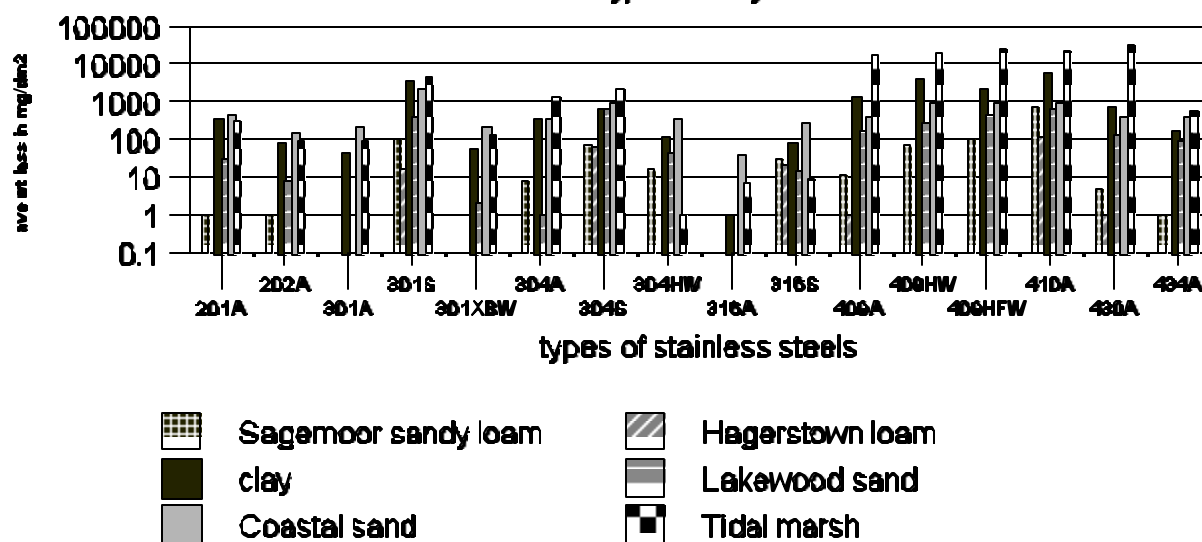


Chart 2b - Corrosion of Stainless Steels

in 6 different soil types for 8 years

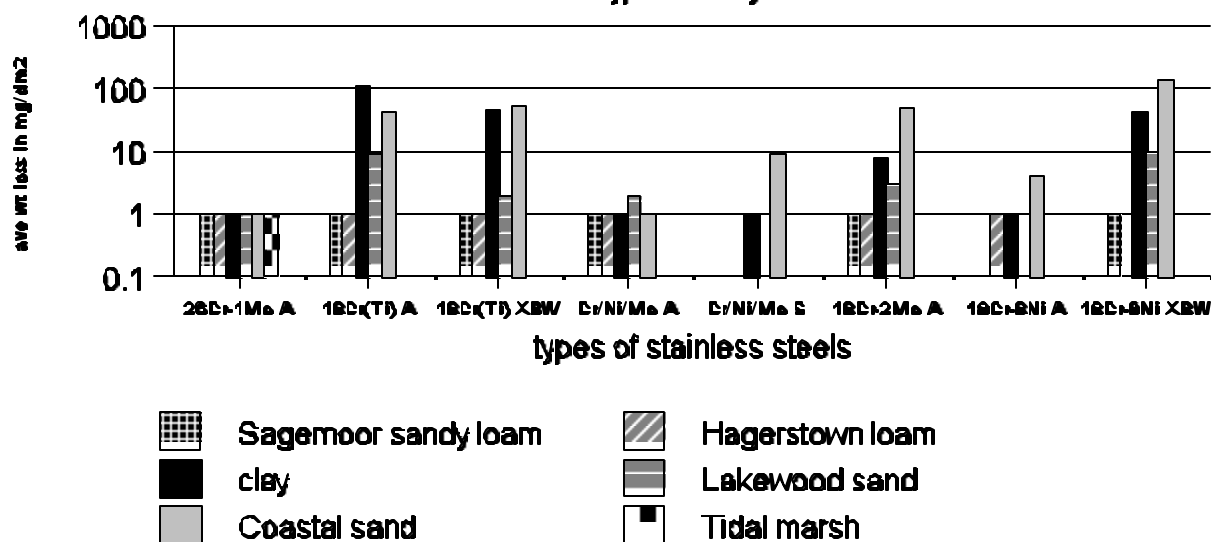
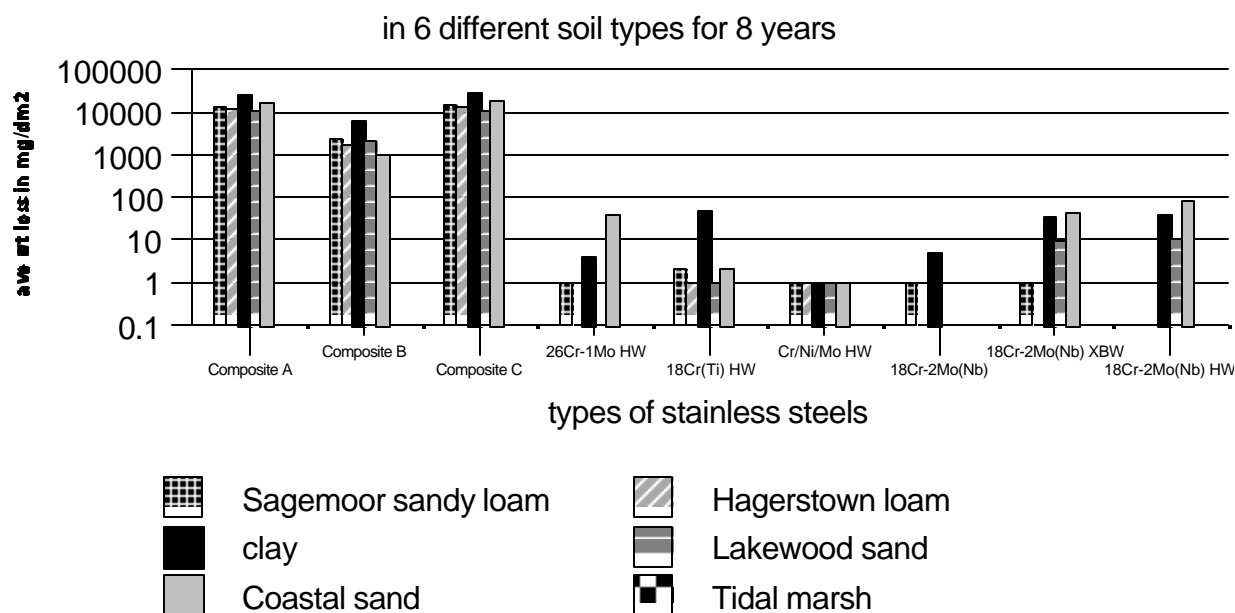


Chart 2c - Corrosion of Stainless Steels



The properties of the above six soil types are summarized in Table 2, followed by a discussion of the characteristics of each site. ^(41,42)

Toppenish, Washington is located outside of the Yakima Valley and is impressively surrounded by distant snow-covered mountains of volcanic origin. The region is semiarid with a rainfall of less than 10 in/yr but supports an abundant growth of sagebrush. The area has a gentle slope leading to a nearby stream which is fed from a spring located about 160 feet from the site. Being a sandy loam in a dry area, the internal drainage is very good. The soil surface layers are dry and powdery and show little evidence of moisture even to a depth of 3 feet. The soil pH is 8.8 and is the most alkaline of the six sites. The average resistivity was over 10,000 ohm-cm but can be as low as 400 ohm-cm when wet. Metals and alloys generally are not seriously affected by corrosion in the high-resistivity soil of this arid region.

Loch Raven, Maryland is located north of Baltimore and within 1.2 miles of a water reservoir. The area is gently rolling, densely wooded hills with a natural cover of weeds and grasses. Rainfall is about 50 in/yr. The soil has good drainage and is made up of a loam to a depth of about 12 inches, which is underlain by a red-brown clay. The pH of the soil is 5.4 and has a redox potential averaging +381 mV, indicating good aeration. The average soil resistivity is about 33,000 ohm-cm. The relatively low pH and clay soil beneath can lead to high corrosion, however, the high resistivity tends to result in low corrosion.

Table 2. Composition of Soil Types

	Sagemoor sandy loam	Hagerstown loam	Clay	Lakewood sand	Coastal sand	Tidal Marsh
Location	Toppenish, Wash.	Loch Raven, Maryland	CapeMay N. Jersey	Wildwood, N. Jersey	Wildwood, N. Jersey	Patuxent, Maryland
mg Ca/ 100 g soil	0.54	*	2.70	*	1.51	0.70
mg Mg/ 100 g soil	0.19	*	6.18	*	2.70	1.35
mg Na/ 100 g soil	8.50	*	9.51	*	13.9	10.2
mg CO ₃ / 100 g soil	0.0	*	0.0	*	0.0	0.0
mg HCO ₃ / 100 g soil	8.20	*	0.0	*	0.09	0.0
mg SO ₄ / 100 g soil	0.45	*	14.0	*	2.36	3.56
mg Cl/ 100 g soil	0.93	*	9.94	*	16.2	9.18
mg NO ₃ / 100 g soil	0.01	*	0.19	*	0.05	0.06

* Analysis was not made for Hagerstown loam and Lakewood sand because of the very low concentration of soluble salts in these soils.

Cape May, New Jersey is located at the mouth of the Delaware Bay facing the Atlantic Ocean. The area is generally flat and devoid of hills. The site, which is a large clay/silt pit, is located about 320 feet from the ocean. Permeability of this clay/silt is so low that rainfall runs off of its surface with little percolation. The pH of this soil is 4.3. The redox potential of this soil fluctuates but tends to be positive at about +215 mV, suggesting a moderately corrosive environment. The soil resistivity is consistently below 1000 ohm/cm with an average of about 600 ohm-cm. The close proximity of the ocean combined with the very low resistivity of the soil makes this a very corrosive site.

The Wildwood, New Jersey sites are very similar except that the coastal sand site is located on

the beach nearest the ocean, while the Lakewood sand site is a few hundred meters inland. These two sites are along the Atlantic Ocean approximately 0.6 miles north of Cape May. Though both are loose sand soils, the site nearest the ocean is often saturated with salt water with poor drainage, while the inland site is rarely, if ever, flooded. The inland site supports an abundant growth of shrubs and grasses. The beach site is beginning to develop a growth of beach grass, which builds and holds dunes in the area. The soil pH of the inland site is 5.6 while the beach site is essentially neutral at 7.1. Both sites exhibit high redox potentials well over +400 mV, indicating good aeration. The soil resistivities at both of these sites fluctuate with time. Their high permeabilities allow soluble salts to wash away during a heavy rainfall, resulting in unusually high resistivities after a rain. The average resistivity for the inland site is 33,000 ohm-cm, while the beach site's average resistivity is 24,000 ohm-cm. The uniformity in the makeup of this soil and the high resistivities tend to make these low-corrosivity soils.

Patuxent, Maryland is situated near the southern tip of Maryland and lies alongside the Chesapeake Bay. The area is hilly and heavily wooded with an abundant growth of weeds and grasses. The site is in a creek estuary, which is commonly flooded during high tide. Its internal drainage is very poor because of the clay type of soil, which holds water, and because of the water table, which is very close to the surface. The pH of the soil is maintained at about 6 by sulfate-reducing bacteria. The redox potential of this soil is negative, indicating poor aeration. Its resistivity is often below 500 ohm-cm. During high tide, the site is exposed to fresh water, which when combined with heavy rainfall, raises the resistivity of the soil. The combined effects of these changing conditions and the presence of anaerobic bacteria make this soil very corrosive.

In the Charts 2a, 2b, and 2c the type of stainless steel is listed first, followed by the type of treatment the stainless steel was given. There were 18 different types of stainless steel tested with six different types of treatment for a total of 34 different alloys. The treatments were: A = annealed; S = sensitized; XBW = cross-bead weld; HW = heliarc weld; HFW = high frequency weld; and HDZ = hot-dip zinc (Zn) coated after bonding. The stainless steels used were: 201, 202, 301, 304, 316, 409, 410, 430, 434, (26% Cr/1% Mo), (18% Cr/<1% Ti), (20% Cr/24% Ni/6.5% Mo), (18% Cr/2% Mo), (18% Cr/8% Ni), (26% Cr/6.5% Ni), (18% Cr/2% Mo/<1% Nb), and three composites [A = carbon steel/type 430/carbon steel], [B = carbon steel/type 430/carbon steel] hot-dip zinc coated after bonding, and [C = carbon steel/type 304/carbon steel]. The seven stainless steels that were treated either with heliarc weld or high frequency weld were tube specimens fabricated from sheet material, welded at the seams, and then plugged and capped at each end to minimize internal corrosion. Specimens of all other systems were flat sheet material.

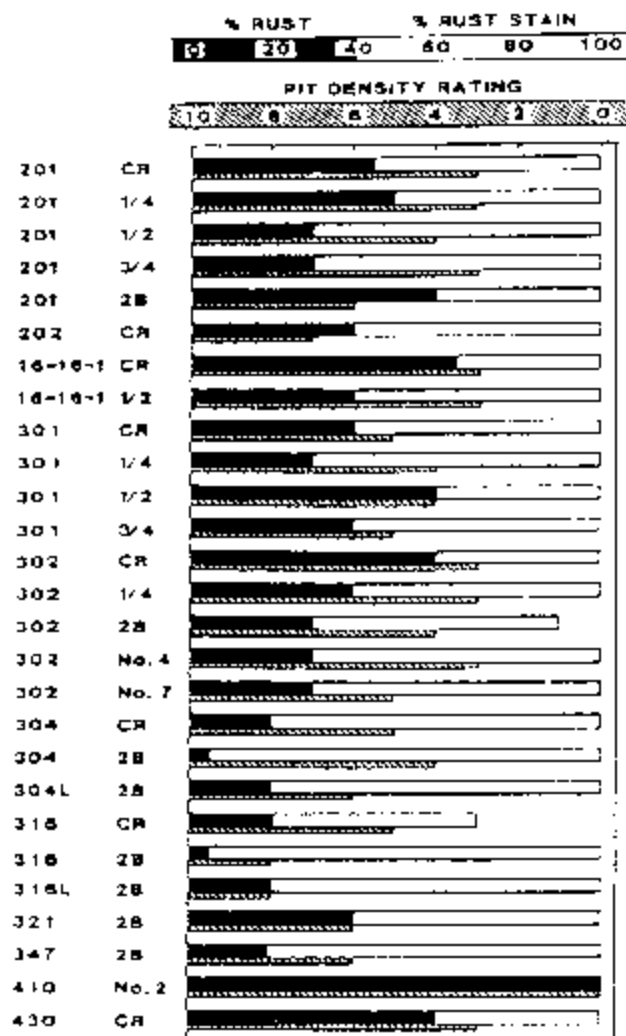
As shown before, the 400 series of stainless steels corrode faster than the 200 series of stainless steels. The stainless steels with high chromium content have the lowest corrosion rates of all the stainless steels tested. The composites corroded faster than all the alloys because the corrosion was occurring where the different types of steel were bonded. This type of corrosion is galvanic corrosion which is driven by the electrochemical potential difference between the two alloys bonded.

In general, all studies showed similar results. Some types of stainless steel corrode slower than other types of stainless steels but given enough time all stainless steels do corrode. Also the rate of corrosion is very different in different types of soil. Tidal marsh, coastal sand, and clay are much more corrosive to stainless steel than loam.

A review of 685 cases of failure of corrosion resistant stainless steel piping and equipment that occurred in the chemical process industry between 1968 and 1971 showed that about 55% of the time (about 377 cases) failure could be attributed to corrosion. The review also showed that the major mode of attack on stainless steels is localized corrosion, i.e., stress corrosion, cracking, pitting, intergranular corrosion, corrosion fatigue, and crevice corrosion. This agrees with the basic results of all corrosion studies on stainless steels; localized corrosion is a major type of corrosion attack.⁽⁴³⁾

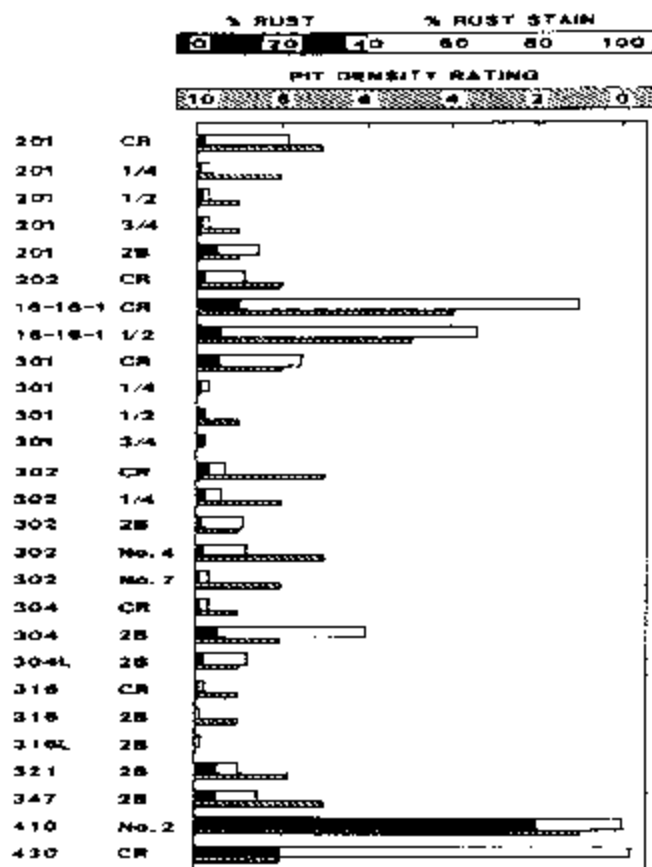
Atmospheric corrosion of stainless steels is well documented. In fact, the rusting of bridges and other types of steels and stainless steels are easily observed in daily life. The atmospheric contaminants most often responsible for the rusting of structural stainless steels are chlorides and metallic iron dust. Chloride contamination may originate from the calcium chloride used to make concrete or from exposure in marine or industrial locations or from the road salt used during inclement weather. Iron contamination may occur during fabrication or erection of the structure. Charts 3a and 3b summarize the results of several studies by E. A. Baker and T. S. Lee that show the relative performance of stainless steels exposed 25 meters and 250 meters from the ocean for 26 years. These studies also show that the 300 series of stainless steels have much higher corrosion resistance than the 400 series.⁽⁴⁴⁾

Chart 3a
Stainless Steels Exposed 25 meters from Ocean for 26 years



Stainless steel. Relative performance of stainless steels exposed 25 m from the ocean for 26 years. Source: E.A. Baker and T.S. Lee, "Long-Term Atmospheric Corrosion Behavior of Various Grades of Stainless Steel," *Degradation of Metals in the Atmosphere* (STP 965), S.W. Dean and T.S. Lee, Ed., ASTM, Philadelphia, 1987, 62.

Chart 3b.
Stainless Steels Exposed 250 meters from Ocean for 26 years



Stainless steel. Relative performance of stainless steels exposed 250 m from the ocean for 26 years. Source: E.A. Baker and T.S. Lee, "Long-Term Atmospheric Corrosion Behavior of Various Grades of Stainless Steel," *Degradation of Metals in the Atmosphere* (STP 965), S.W. Dean and T.S. Lee, Ed., ASTM, Philadelphia, 1987, 63.

In general, austenitic steels have a higher degree of corrosion resistance than the martensitic or ferritic steels. The molybdenum-bearing austenitic grades have the greatest resistance among the austenitic grades.

All stainless steels are resistant to most concentrations of nitric acid and non-chloridic oxidizing acids in general, with the austenitic grades demonstrating the highest resistance. The molybdenum-bearing grades resist many organic acids and organic bases (e.g., amines) under a variety of process conditions. All stainless steels lose passivity and corrode actively in reducing mineral acids such as

hydrofluoric, hydrochloric, and dilute sulfuric acid, although oxidizing contaminants can mitigate corrosion. Caustic environments are noncorrosive at ambient temperatures but can cause stress-corrosion cracking at elevated temperatures and active corrosion in high concentrations (e.g., 40-50% NaOH above 80 °C).

Non-halide salts have little effect on stainless steels, but chlorides particularly tend to promote pitting, crevice corrosion, and stress-corrosion cracking. In some cases sulfates seem to aggravate the effects of chlorides. Chlorides present in amounts as little as 0.3% with sulfates present can produce severe corrosion. Even quite low concentrations of chlorides can cause corrosion when concentrated by occlusion in surface films. Oxidizing chlorides such as ferric or cupric chloride are specific for severe pitting, although halide salts can cause severe pitting and stress corrosion cracking. The austenitic stainless steels are, however, the most susceptible of all the stainless steels to “chloride” stress corrosion cracking.

In high temperature applications, all grades of stainless steels are severely attacked by fuel ash containing vanadium or chlorides, with or without sulfates. Fuels containing only 50 ppm vanadium can produce severe attack on all grades of stainless steels.⁽⁴⁵⁾

An excellent summary of corrosion studies of stainless steels in and near water is presented in Chapter 4 of “Corrosion of Metals in Marine Environment - A State of the Art Report.”⁽⁴⁶⁾ All of the studies show that, depending on the type of stainless steel and the conditions to which it is exposed, most stainless steels will corrode.

VIII. Microbiologically Induced Corrosion (MIC)

Reports of accelerated corrosion of stainless steels associated with microorganisms began to appear in the early 1970s. Many of these reports did not give the specific type of organism involved in MIC, but rather only indicated that bacteria or some other microorganism could be identified as a possible cause of the corrosion problems. In the early 1980s papers were published that began to describe MIC in more detail.⁽⁴⁷⁾

Microbial slime layers, known as biofilms, form over a period of days on all solid surfaces when the surfaces are exposed to an aqueous environment containing microbes. These biofilms are living entities that, through their metabolism, produce major changes in the solution chemistry at the surface of the stainless steel. Three of the main types of bacteria associated with pitting attack on stainless steels are: (1) aerobic iron- and manganese-oxidizing bacteria (*Gallionella*, *Siderocapsa*, *Sphaerotilus*), (2) anaerobic sulfate-reducing bacteria (*Desulfovibrio*, *Desulfotomaculum*), and (3) aerobic iron- and sulfur-oxidizing bacteria (*Thiobacillus ferrooxidans*). The iron- and manganese-oxidizing bacteria oxidize ferrous (Fe^{2+}) and manganous (Mn^{2+}) ions to their ferric (Fe^{3+}) and manganic (Mn^{3+}) states, respectively. Sulfate-reducing bacteria reduce sulfate (SO_4^{2-}) to sulfide (S^{2-}) and hydrogen sulfide

(H₂S). The iron- and sulfur-oxidizing bacteria oxidize ferrous (Fe²⁺) to ferric (Fe³⁺) and sulfur to sulfuric acid (H₂SO₄), respectively.⁽⁴⁸⁾

The process of biofilm formation begins immediately upon immersion of the metal in the liquid environment. The first step is the adsorption of a nonliving macromolecular organic film. The “conditioning film” is nearly complete within the first two hours of immersion in natural waters at 25 °C. The initially colonizing bacteria also begin to attach in substantial numbers within the first two to four hours of immersion in natural fresh, brackish, and sea waters. This bacterial biofilm usually becomes well developed with the first 48 hours of immersion, although further changes in the film can be observed for a period of two weeks or more depending on the temperature. Once formed, a microbial biofilm changes the chemistry at the metal-liquid interface in a number of ways that have an important bearing on the corrosion. As the biofilm grows, the bacteria in the film produce a number of metabolic by-products, among these are organic acids, hydrogen sulfide, and protein-rich polymeric materials, commonly called exopolymers, or “slime.” The first effect of the composite film of microorganisms and their associated exopolymers is to create a barrier between the metal surface and the bulk electrolyte. Since the biofilm itself is mostly water, it does not truly isolate the interface from the bulk environment, but it does support larger chemical concentration gradients perpendicular to the metal surface than would be supported by the liquid alone. Thus, the water chemistry at the interface may be quite different from that of the bulk solution, although the two chemistries will be coupled through diffusive processes.

Two chemical species, oxygen and hydrogen, that are often implicated or even rate controlling in corrosion, are also important in the metabolism of microorganisms. A biofilm can be a source or a sink for either oxygen or hydrogen. Moreover, biofilms are rarely homogeneous. Sometimes they provide only spotty coverage of the metal surface. Even when they provide nominally complete coverage, their thickness and composition may vary from point to point along the surface.

Large changes in pH are also possible under biofilms. Values as low as 5 can be expected under general aerobic films containing acid producing bacteria. Even more acid pH in the range of 1 to 2 can be expected under discrete biodeposits and pH of 3 is thought to be required for some of the effects produced by marine biofilms on passive alloys in seawater. Some microbes are capable of directly producing acids such as formic, succinic, acetic, and sulfuric, while others are involved in metabolizing nitrogen compounds. Some can reduce nitrates (used as corrosion inhibitors) to nitrite and nitrogen. Others can convert between nitrate and ammonia compounds, which can cause stress corrosion cracking in copper alloys. Still other species of bacteria are involved in the sulfur cycle. Some can oxidize sulfur or sulfides to sulfate, and ultimately to sulfuric acid. Others, particularly the anaerobic sulfate reducing bacteria (SRB) can reduce sulfates to sulfides, often producing corrosive hydrogen sulfide as an end product. Many of these organism have both fresh and salt water strains. Organisms with a fermentative metabolism can be net producers or consumers for the dissolved gases, carbon dioxide and hydrogen.

In all of these examples, the biofilm is able to substantially change the chemistry of the electrolyte at the metal-water interface. Thus, the corrosion rate may depend more on the details of the electrolyte chemistry at the interface under the biofilm than it does on the bulk environment chemistry. The fact that biofilms tend to be spatially heterogeneous allows them to support sharp chemistry gradients both parallel and perpendicular to the metal surface. This is one of the reasons why corrosion tends to become more localized in the presence of microorganisms. Also there is a tendency for the biofilms to develop and change with time. This can produce corrosion rates which also vary with time.⁽⁴⁹⁾

Of the microorganisms identified with the corrosion of stainless steel, aerobic iron and manganese oxidizing bacteria and another microbial species, *Bacillus* spp have been implicated in the pitting and stress-cracking of type 304 and 316 stainless steels in hot (75-90 °C) demineralized water containing about 20 ppm chloride. Chloride accumulation at surface deposits caused by microbe colonizations was identified as the cause of the pitting and cracking. In these cases it was believed that the bacteria oxidized ferrous (Fe^{2+}) and manganous (Mn^{2+}) ions to ferric (Fe^{3+}) and manganic (Mn^{3+}) ions, which when combined with ambient chlorides, resulted in the corrosion.⁽⁵⁰⁾ MIC is a significant problem in soils and in wastewater treatment plants where bacteria and organic compounds are readily available. There are few materials known to be resistant to MIC.

There are few reported observations of sulfate-reducing bacteria (SRB) involved with the corrosion of stainless steels. Two cases of extensive corrosion in chemical process industry environments involving stainless steels 303 and 304 have been reported. Several reports of similar cases have been found in the pulp and paper industries. Both SRB and *Sphaerotilus* were identified. The results suggested that corrosion of the stainless steel may have occurred due to oxygen and/or acid concentration cells created by sludge build-up. It was suggested that the slime formers set up anaerobic conditions in which the metabolic products of the microorganisms accumulated and acted to destroy the passive film. Other studies have indicated no effect of the SRB in the absence of slime on corrosion of stainless steels.⁽⁵¹⁾

Brasses and bronzes have long been known for their ability to resist fouling in seawater. It is known that copper and copper alloys produce corrosion products, i.e., copper ions, that are toxic to marine organisms and therefore suppress the attachment of these fouling organisms. However, many bacteria may tolerate very high levels of copper. For example, *Thiobacillus thiooxidans* can withstand copper concentrations as high as 2%. It is interesting to note that bacteria can play a central role in leaching copper for low-grade ores, a fact that has been used in microbiological mining.⁽⁵²⁾

There are several ways that bacterial action can cause corrosion: (1) by direct action, e.g., by the production of corrosive substances such as carbon dioxide, hydrogen sulfide, ammonia, organic or inorganic acids; (2) by metabolic production of organic products that can act as depolarizers or catalysts of corrosion reactions; and (3) in cases similar to the anaerobic corrosion of iron, by the activities of the sulfate-reducing organisms where, under some conditions, the corrosion reaction is an

integral part of the metabolic cycle of the bacteria. The theory is that the acceleration of corrosion by bacteria is based on the fact that hydrogen acceptors and oxidation-reduction systems, set up during bacterial metabolism, are present at the surface of the metal. For the disulfide-mercaptan system, it was suggested that depolarization might well be the mechanism of corrosion.

Under anaerobic conditions, sulfate-reducing bacteria (SRB) were found to have an adverse effect on copper and its alloys as a consequence of the hydrogen sulfide formed by the bacteria. Bacteriologically produced hydrogen sulfide has been identified in underground corrosion of copper pipes.⁽⁵³⁾

In a study on putrid seawater as a corrosive medium, exposure to fresh seawater under turbulent conditions subsequent to long exposure to putrid seawater, accelerated the corrosion of copper-based alloys. The presence of animal macro-organisms in the putrid seawater generally resulted in higher sulfide levels and lower pHs than did those of plants. In either case the sulfide level was higher than in clean seawater. The pH decreased prior to a rapid sulfide increase when macro-fouling organisms were present. The combined presence of sulfur, microorganisms and corrosion suggests MIC since sulfur and/or its compounds are involved in bacterial metabolism, which is intimately connected with the sulfur cycle in nature. Copper alloy (90 Cu/10 Ni) specimens showed a dramatic increase in their corrosion rates when exposed to aerated, sulfide-polluted seawater as compared to both aerated, unpolluted seawater and deaerated sulfide-polluted seawater. The sulfide seemed to prevent a protective oxide film from forming on the metal. When the copper alloy specimen is subsequently exposed to aerated, unpolluted seawater, this corrosion product still interferes with the formation of the normally protective oxide film that forms on the metal surface. Although there is no consensus on the mechanisms involved, there is consensus that putrid seawater accelerates corrosion of copper alloys.⁽⁵⁴⁾

Mechanistic studies of MIC, using electrochemical techniques, have led to a greater understanding of the corrosion processes involved and helped to link MIC with other forms of corrosion.

IX. Copper and Copper Alloys

Copper and copper alloys have been widely used for centuries in many applications because of their excellent corrosion resistance. Despite the formation of the common green patina in natural environments, copper and its alloys corrode at negligible rates in unpolluted water or air and in deaerated nonoxidizing acids. Copper roofing in rural atmospheres, where there is little if any pollution, has been found to corrode at rates of less than 0.4 mm (15 mils) in 200 years. Some copper alloy artifacts have been found in nearly perfect condition, with only small amounts of corrosion on the surface, after having been buried in the earth for thousands of years.

Copper and high copper alloys have similar corrosion resistance. Atmospheric exposure, fresh water, salt or sea water, and many types of soils can cause uniform corrosion of copper alloys. Pitting corrosion may occur over the entire surface or be localized in a specific area. This type of attack usually occurs at surfaces on which an incomplete protective film exists or at external surface contaminants such as dirt. In marine applications copper and high copper alloys show resistance to seawater corrosion and biofouling, but are susceptible to impingement or erosion attack at high water velocities. This type of attack can occur when liquids or gases impact the metal surfaces at high velocity. The corrosion rate is high under such circumstances because any corrosion product films that can be protective are swept away as quickly as they are formed to leave a fresh exposed surface. Under stagnant anaerobic conditions sulfate-reducing bacteria activity promotes pitting by destroying the protective film developed by flowing aerated seawater.

Copper alloys are resistant to many, but not all, saline solutions, neutral or slightly alkaline solutions, except those containing ammonia, or amines in the presence of oxygen. Strong alkalis will dezincify susceptible brasses and corrode copper alloys when strongly oxidizing contaminants, e.g., chlorates, are present. In strongly reducing conditions at temperatures from 290-400 °C copper alloys are often superior to stainless steels and other stainless alloys.

Although classed as corrosion resistant, neither copper nor its alloys form the truly passive corrosion-resistant film that characterizes most true corrosion-resistant alloys. In aqueous environments at ambient temperatures, cuprous oxide or cupric carbonate forms the protective scale on copper and copper alloys. The film is adherent and follows parabolic growth kinetics. For the corrosion reaction to proceed, copper ions and electrons must migrate through the cuprous oxide or cupric carbonate layer. Consequently, reducing the ionic or electronic conductivity of the film by doping with divalent or trivalent cations should improve corrosion resistance. In practice alloying additions of aluminum, zinc, tin (Sn), iron, and nickel are used to dope the corrosion product films, resulting in a significant reduction in corrosion rate.

Copper alloys can be quite susceptible to stress-corrosion cracking. While high-zinc yellow brasses are the most susceptible to stress-corrosion cracking, small amounts of phosphorus, arsenic (As), antimony (Sb), silicon, aluminum, or nickel as constituents in other copper-base alloys render them also susceptible to stress-corrosion cracking in ammoniacal environments. Other nitrogenous environments, such as nitrite or nitrate solutions, as well as nitric acid vapors, can also cause stress-corrosion cracking. As for other elements, the corrosion-resistant behavior of copper is best revealed by considering its alloy systems. The basic systems for copper are copper-tin (bronze), copper-zinc (brass), copper-nickel (cupro-nickels), and variations of these, including aluminum-bronzes, phosphor-bronzes, and nickel-silvers.⁽⁵⁵⁾

Copper and its alloys are classified in the United States by composition according to Copper Development Association (CDA) designations which have been incorporated into the Unified Numbering System (UNS) for metals and alloys. Wrought copper materials are assigned five digit

numerical designations which range from C10100 through C79999, but only the first three or sometimes four numerals are frequently used for brevity. Designations that start with 8 or 9 are reserved for cast copper alloys.

Most wrought alloys are provided in conditions that have been strengthened by various amounts of cold work or heat treatment. Cold worked alloys are the result of cold rolling or drawing by prescribed amounts of plastic deformations from the annealed condition. Alloys that respond to strengthening by heat treatment are referred to as precipitation or age hardenable. The designations and principal alloying elements of wrought copper alloys are given in Table 3.⁽⁵⁶⁾

Table 3. UNS (CDA) Designations for Copper Alloys

Alloy group	UNS (CDA) designation	Principal alloy elements
Brasses	C20500-C28580	Zn
Leaded brasses	C31200-C38590	Zn-Pb
Tin brasses	C40400-C40980	Sn, Zn
Phosphor bronzes	C50100-C52400	Sn-P
Leaded bronzes	C53200-C54800	Sn-P, Pb
Phosphorus-silver	C55180-C55284	Ag-P
Aluminum bronze	C60600-C64400	Al, Fe, Ni, Co, Si
Silicon bronze	C64700-C66100	Si, Sn
Modified brass	C66400-C69950	Zn, Al, Si, Mn

Zinc content in copper can range from a few percent to about 40%. The resistance of brasses to corrosion does not change markedly as long as the zinc content is 15% or less. When the zinc content exceeds 15%, the alloy may be susceptible to dezincification. This is a process involving the leaching of the zinc from the alloy. It results in a porous, reduced ductility, reddish copper matrix. High zinc content introduces the possibility of stress-corrosion cracking. Very high zinc content, as in Muntz metal, may lead to excessive corrosion attack in seawater due to dezincification. Limited or no data are available on the effects of zinc in brasses on the rate of corrosion; however, the addition of tertiary and quaternary elements is known to enhance the resistance of zinc-containing alloys to certain environments.

Nickel and copper are mutually soluble or miscible. In commercial alloys known as copper-nickels or cupronickels, where copper is the dominant element, the copper content ranges from about 54% to over 90%. Nickel provides the best general resistance to aqueous corrosion of all the commercially important alloy elements. It promotes resistance to impingement or erosion corrosion and to stress corrosion cracking. The addition of 10-25 wt% nickel to copper-zinc alloys produces alloys called nickel-silvers. Most commonly these have about 18% nickel and 55-65% copper. Such alloy additions promote good resistance to corrosion in both fresh and salt waters. The nickel inhibits dezincification. Nickel-silvers are much more corrosion resistant in saline solutions than brasses of similar copper content.

Other elements are added to copper alloys in varying amounts to enhance corrosion resistance. For example, the addition of arsenic, antimony, or phosphorus improves resistance of Admiralty Metals (72% copper, 26% zinc, 1% tin) to dezincification. Also, 2% aluminum is added to 76% copper-22% zinc solutions to produce aluminum brass, and a small amount of arsenic (less than 0.10%) is added to the alloy to inhibit dezincification.⁽⁵⁷⁾

X. Specific Properties of Copper Wrought Alloys⁽⁵⁸⁾

Copper Alloys

Copper alloys can be grouped according to how the principal elemental additions affect properties. This grouping depends primarily on whether the additions that dissolve in the liquid copper can form discrete second phases during melting/casting or in-process thermal treatment. Alloys are considered to be a solid solution alloy when copper dissolves other elements to varying degrees to produce a single-phase alloy that is strengthened relative to unalloyed copper. The contribution to strengthening from an element depends on the amount of the element in solution and by its particular physical characteristics, such as atom size and valency. Tin, silicon, and aluminum show the highest strengthening efficiency of the common elemental additives, whereas nickel and zinc are the least efficient. The limiting factor in their alloy range is the extent to which the elements, either singly or in combination, remain dissolved in the copper during processing. Table 4 gives the designations and compositions of some copper wrought alloys.

The presence of finely dispersed second-phase particles in copper alloys contributes to strength, through refined grain size and increased response to hardening from cold working. A dispersion of fine particles can be incorporated into the alloy through thermomechanical processing where the alloy content is above the solid state solubility limit. Precipitation and coarsening of the excess solute by an in-process anneal is used in high copper alloys, such as C194 and C195, to form iron or iron-cobalt dispersions.

Table 4. UNS (CDA) Designation and Compositions of some Copper Wrought Alloys⁽⁵⁹⁾

Alloy group	UNS designation	Elemental composition, wt% ^a
Zinc brass	C260	30 Zn
Leaded brass	C360	35 Zn, 3 Pb
Tin brass	C425	9.5 Zn, 2.0 Sn
Phosphor bronze	C510	5.0 Sn, 0.1 P
Aluminum bronze	C638	2.8 Al, 1.8 Si
Silicon bronze	C654	3.0 Si, 1.5 Sn, 0.1 Cr
Silicon bronze	C655	3.3 Si, 0.9 Mn
Modified Cu-Zn	C688	22.7 Zn, 3.4 Al, 0.4 Co

^aRemaining percentage is copper.

Powder metallurgy is used to incorporate second phases into copper. Aluminum oxide powder that otherwise does not dissolve in copper is incorporated in C15720 by mixing powders of copper, copper oxide particles, and a dilute copper-aluminum alloy. Hot extrusion is used to consolidate the mixture. Subsequent heat treatment allows copper oxide to react with dissolved aluminum in the alloy powder to form uniformly dispersed submicrometer sized aluminum oxide particles within the alloy. It is this ultra-fine oxide that is principally responsible for the alloy's resistance to softening during subsequent high temperature exposure.

Copper-Zinc Brasses

Copper-zinc alloys have been the most widely used of the copper alloys during the 1990's. Brass alloys fall within the designation C205 to C280 and cover the entire solid solution range up to 35 wt% zinc in the Cu-Zn alloy system. Zinc, which is generally less expensive than copper, does not impair conductivity and ductility to any appreciable extent. The alloys have a yellow "brass" color at zinc levels above 20 wt%. By far the best known and most used composition is the 30 wt% zinc alloy, called Cartridge brass, which is best known for its applications as door knobs and bullet cartridges.

The series of brasses, C312 to C385, contain from 0.25-5.0 wt% lead (Pb) for the purpose of improving machinability. C360, having the composition of 61.5 wt% copper, 35.4 wt% zinc, and 3.1 wt% lead, has become the industry standard for machinability performance.

Brasses are susceptible to dezincification in aqueous solutions when they contain > 15 wt% zinc. Stress corrosion cracking susceptibility is also significant above 15 wt% zinc. Over the years,

other elements have been added to improve corrosion resistance. For example, a small addition of arsenic or phosphorus helps prevent dezincification making brasses more useful in tubing applications.

Tin Brass

The tin brass series of alloys consists of various copper-zinc (2.5-35 wt%) alloys to which up to about 4 wt% tin has been added. These are the C40000 series of alloys. Tin provides better general corrosion resistance and strength without greatly reducing electrical conductivity. Several tin brasses have lead additions to enhance machinability. Naval Brass C485 contains 60.5 wt% copper, 37 wt% zinc, 0.7 wt% tin, and 1.8 wt% lead. Resistance to dezincification is increased with the addition of tin. In copper alloys that contain a high zinc content, it is common to use other alloying additives to enhance corrosion resistance. C443 contains 0.02-0.10 wt% arsenic, C444 contains 0.02-0.10 wt% antimony, and C445 contains 0.02-0.10 wt% phosphorus, which is added to control dezincification. When any of these elements are used, the alloy is referred as being “inhibited.”

Tin Bronzes

Tin bronzes may be the most familiar of copper alloys with roots going back into ancient times. They are essentially solid solutions of tin in copper. Phosphorus at 0.03-0.35 wt% is commonly used as a deoxidizer, and the residual phosphorus content gives rise to the term “phosphor bronze.” The addition of tin to copper promotes good resistance to fresh and sea water. Under some conditions, when more than 5% tin is present, the corrosion resistance in marine applications is enhanced. Strength, corrosion resistance, and stress relaxation resistance increases with tin content. Where the water velocity is high, the tin content in copper alloys for marine applications should exceed 5%. Alloys containing between 8-10% tin have high resistance to impingement or erosion attack. Tin bronzes tend to have intermediate pitting resistance. One of the most highly used specialty tin bronzes is C544, containing 88 wt% copper-4 wt% tin-4 wt% zinc-4 wt% lead. Zinc provides increased strength to this tin bronze, whereas the lead addition provides good machinability.

Aluminum Bronzes

Aluminum bronze alloys comprise a series of alloys (C606 to C644) based on the copper-aluminum (2-15 wt%) binary system, to which iron, nickel, and/or manganese are added to increase strength. Corrosion resistance results from the formation of an adherent aluminum oxide layer that protects the surface from further oxidation. Mechanical damage to the surface is readily healed by the redevelopment of this oxide. The aluminum bronzes are resistant to sulfuric or hydrochloric acids, but not nitric acid. These alloys must be properly heat treated to be resistant to dealloying and general corrosion.

Two single-phase, binary alloys are used commercially: C606, containing 5 wt% aluminum and C610, containing 8 wt% aluminum. Most of the available aluminum bronzes contain additional alloy elements. C608 contains 5 wt% aluminum to which 0.02-0.35 wt% arsenic has been added to improve corrosion resistance. Alloy C614, in addition to having 7 wt% aluminum and 2.5 wt% iron, also has a 0.3 wt% tin addition for improved resistance to stress corrosion.

Most of the aluminum bronzes contain substantial iron, nickel, or manganese additions. These alloying elements increase strength by forming second phases during heat treatment. Iron, the most commonly added element, separates as an iron-rich particle that controls grain size while it enhances strength. Nickel also reacts with aluminum to form NiAl precipitated during heat treatment with the same result as the iron addition.

Silicon Bronzes

Silicon bronzes have long been available for use in electrical connectors, heat exchange tubes, and marine and pole line hardware because of their high solution hardened strength and resistance to general and stress corrosion. Their compositions are limited to below 4.0 wt% silicon because above this level, an extremely brittle phase is developed that prevents cold processing. The three most popular alloys in this series are C651, C654, and C655.

Modified Copper-Zinc Alloys

The series of copper-zinc base alloys (C664 to C698) have been modified by additions of manganese (manganese bronzes and manganese bronzes), aluminum, silicon, nickel, and cobalt. Each of the modifying additions provides some property improvement to the already workable, formable, and inexpensive Cu-Zn brass base alloy. Aluminum and silicon additions improve strength and corrosion resistance. Nickel and cobalt form aluminide precipitates for grain size control and dispersion strengthening by the presence of finely dispersed second-phase particles in the copper alloy.

Precipitation-Hardening Alloys

Copper alloys that can be precipitation hardened to high strength are limited in number. Those that can be precipitation hardened have the constitutional characteristics of being single-phase (solid solution) at elevated temperatures and are able to develop into two or more phases at lower temperatures. In addition to the metallurgical requirement that the solubility of the added element(s) decrease with temperature, the precipitated phase that forms during aging must be distributed finely and have characteristics that act to resist plastic deformation. Commercial precipitation hardening copper alloys are based on beryllium (Be), chromium, and nickel, this last in combination with aluminum, tin, silicon, or zirconium. The principal attributes of these alloys are high strength in association with adequate formability.

XI. Specific Properties of Cast Copper Alloys⁽⁶⁰⁾

Cast copper alloys can be classified into two main groups: single-phase alloys, characterized by moderate strength, high ductility (except for leaded varieties), moderate hardness and good impact strength; and polyphase alloys, having high strength, moderate ductility, and moderate impact strength. The tolerance for impurities is normally greater in cast copper alloys than in wrought copper alloy because the cast alloys are not mechanically formed. However, in those cast alloys likely to be repaired

or joined by welding, some impurities can be very detrimental. On the basis of consumption, red brass alloys, C83600 (85 wt% copper, 5 wt% tin, 5 wt% lead, and 5 wt% zinc), C84400 (81 wt% copper, 3 wt% tin, 7 wt% lead, and 9 wt% zinc), and C93200 (83 wt% copper, 7 wt% tin, 7 wt% lead, and 3 wt% zinc) are the most important of the cast copper alloys.

The mechanical properties of cast copper alloys are a function of alloying elements and their concentrations. The nominal chemical composition and identification of some copper casting alloys are listed in Table 5.⁽⁶¹⁾

Table 5. Nominal Composition by wt% of Some Casting Copper Alloys

Common name	UNS (CDA) designation	Cu	Sn	Pb	Zn	Fe	Al	Others
high strength yellow brass	C86300	63.0			25.0	3.0	6.0	3.0 Mn
gun metal	C 90500	88.0	10.0		2.0			
tin bronze 84:16	C 91100	84.0	16.0					
high leaded tin bronze	C 93700	80.0	10.0	10.0				
steam bronze	C 92200	88.0	6.0	1.5	4.5			
phosphorus bronze	C 94400	81.0	8.0	11.0				0.35 P
high leaded tin bronze	C 93800	78.0	7.0	15.0				
journal bronze	C 94100	70.0	5.5	18.0	3.0			
aluminum bronze 9D	C 95500	81.0				4.0	11.0	4.0 Ni
Al-Silicon bronze	C 95600	91.0					7.0	2.0 Si
Mn-Al bronze	C 95700	75.0				3.0	8.0	12.0 Mn, 2.0 Ni
Ni-Al bronze	C 95800	81.0				4.0	9.0	1.0 MN, 5.0 Ni

Common name	UNS (CDA) designation	Cu	Sn	Pb	Zn	Fe	Al	Others
die-casting yellow brass	C 85800	58.0	1.0	1.0	40.0			
die-cast silicon brass	C 87800	82.0			14.0			4.0 Si
commercial no. 1 yellow brass	C 85400	67.0	1.0	3.0	29.0			
yellow brass	C 85700	63.0	1.0	1.0	34.7		0.3	
high strength yellow brass	C 86200	64.0			26.0	3.0	4.0	3.0 Mn
leaded high strength yellow brass	C 86400	59.0		1.0	40.0	2.0	1.5	1.5 Mn
silicon bronze	C 87200	89.0	1.0	0.5	5.0	2.5	1.5	1.5 Mn, 4.0 Si
silicon brass	C 87400	83.0			14.0			3.0 Si
silicon brass	C 87500	82.0			14.0			4.0 Si
tin bronze	C 90300	88.0	8.0		4.0			
leaded tin bronze	C 92300	87.0	8.0	1.0	4.0			
high leaded tin bronze	C 93200	83.0	7.0	7.0	3.0			
nickel-tin bronze	C 94700	88.0	5.0		2.0			5.0 Ni
leaded nickel-tin bronze	C 94800	87.0	5.0	1.0	2.5			5.0 Ni

The mechanical properties of cast copper alloys are a function of alloying elements and their concentrations. The specific effects of a number of these alloying elements are presented below.⁽⁶²⁾

Aluminum

Aluminum added as the principal alloying element to copper forms a series of high strength alloys called aluminum bronzes. Aluminum forms solid solutions with copper up to about 9.5 wt%. High strength yellow bronzes contain aluminum in varying amounts.

Arsenic and Antimony

Arsenic and antimony can be added in small quantities, up to about 0.05 wt%, to all brass alloys containing less than 80% copper to inhibit the dezincification types of corrosion in yellow brass alloys.

Beryllium

Beryllium added to copper forms a series of age- or precipitation-hardenable alloys. These heat-treatable alloys are the strongest of all known copper-base alloys.

Chromium

Chromium added to copper forms heat-treatable copper alloys.

Iron

Iron added to copper alloys adds strength to the silicon, aluminum, and manganese bronzes. It combines with aluminum or manganese to form hard, intermetallic compounds. Undissolved iron in the alloy leads to nonuniform hardness and interferes with machining.

Lead

Lead is added to copper in amounts up to 40 wt%. Lead is insoluble in copper-based alloys and because of its low melting point is found distributed in the grain boundaries of the casting. Because lead imparts a certain degree of brittleness to the structure, it enhances machining operations by causing the alloy to break into chips as cutting tools are thrust into the matrix. Additions of lead up to 1.5 wt% significantly improve machinability without a serious decrease in tensile strength. Lead concentrations of 5-25 wt% greatly increase machinability of the alloy but with a resulting decrease in tensile strength. Alloys with lead concentrations equal to or greater than the tin content are used for bearing applications requiring resistance to both wear and friction. Lead added to copper in amounts of about 35-40 wt% forms a useful bearing alloy. However, lead is considered undesirable in high strength manganese bronze, silicon bronze, and silicon brass. It affects the surface of silicon bronze and silicon brass, causing noticeable darkening and pockmarking.

Manganese

Manganese is added as an alloying element in high strength bronzes where it forms compounds with other elements such as iron and aluminum. Manganese may also be used as a deoxidizer, although it is not a common usage.

Nickel

Nickel added to copper markedly whitens the resulting alloy. Cupronickel alloys contain 10-30 wt% nickel and have very high corrosion resistance. Iron, up to a nominal 1.4 wt%, added along with nickel significantly enhances the resistance toward impingement corrosion. Added to bronzes, nickel refines the cast grain structure and adds toughness. Nickel improves strength and corrosion resistance. An alloy series containing 10-25 wt% nickel, along with tin, lead, and zinc as principal alloying elements, is known as the nickel-silvers. Nickel is added up to about 1 wt% to some of the high tin-gear bronze alloys to enhance wear properties.

Phosphorus

Phosphorus is used principally as a deoxidizer in copper and high copper alloys. The alloy should contain a minimum residual of 0.02 wt% phosphorus to ensure complete deoxidization. Lesser amounts of residual phosphorus can form an equilibrium system with copper and oxygen. Phosphorus can be added in small quantities, up to about 0.05 wt%, to all brass alloys containing less than 80 wt% copper to inhibit the dezincification types of corrosion in yellow brass alloys.

Silicon

Alloys of high strength and toughness along with improved corrosion resistance, particularly in acidic media, result when silicon is added to copper. Silicon in small amounts can improve fluidity.

Tin

Tin added to copper in concentrations of 5-20 wt% forms the tin-bronze alloys series. Leaded tin bronze is also produced. Typically a deoxidizer is added to the melt to produce a clean structure. Tin imparts strength and hardness to copper-base alloys, making them tough and wear resistant. It also enhances the corrosion resistance of copper-base alloys in nonoxidizing media. Small amounts of tin, 3-5 wt%, are added to leaded red brass and semi-red bronzes to increase the strength and hardness of the alloys. In high tensile strength manganese-bronze, tin is limited to a maximum of 0.2 wt% as it lowers the tensile strength and ductility of the alloy.

Zinc

Zinc is added to copper as a principal alloying element in concentrations of 5-40 wt%, forming the alloy series known as bronzes. Zinc increases the tensile strength at a significant rate up to a concentration of about 20 wt%, then the tensile strength increases only slightly more for additions of 20-40 wt% zinc. Zinc up to 5 wt% is added to tin bronze alloys to tighten the structure and to act as a deoxidizer. In yellow bronzes zinc imparts a freedom from gas porosity because when the melt is heated until the zinc boils, the zinc vapors sweep the melt free of gas.

Cast copper-zinc alloys are described as red bronzes and leaded red bronzes, semi-red, silicon, yellow and high strength yellow bronzes. Red bronzes and yellow bronzes contain zinc as the principal alloying element, along with some tin and lead or other designated elements; however, yellow bronzes contain significantly more zinc than the red bronzes. Semi-red bronzes contain less copper than do red

brasses. High strength yellow brasses are alloys that contain zinc with smaller amounts of iron, aluminum, nickel, and lead.

XII. General Corrosion of Copper Alloys, i.e., Brass and Bronze

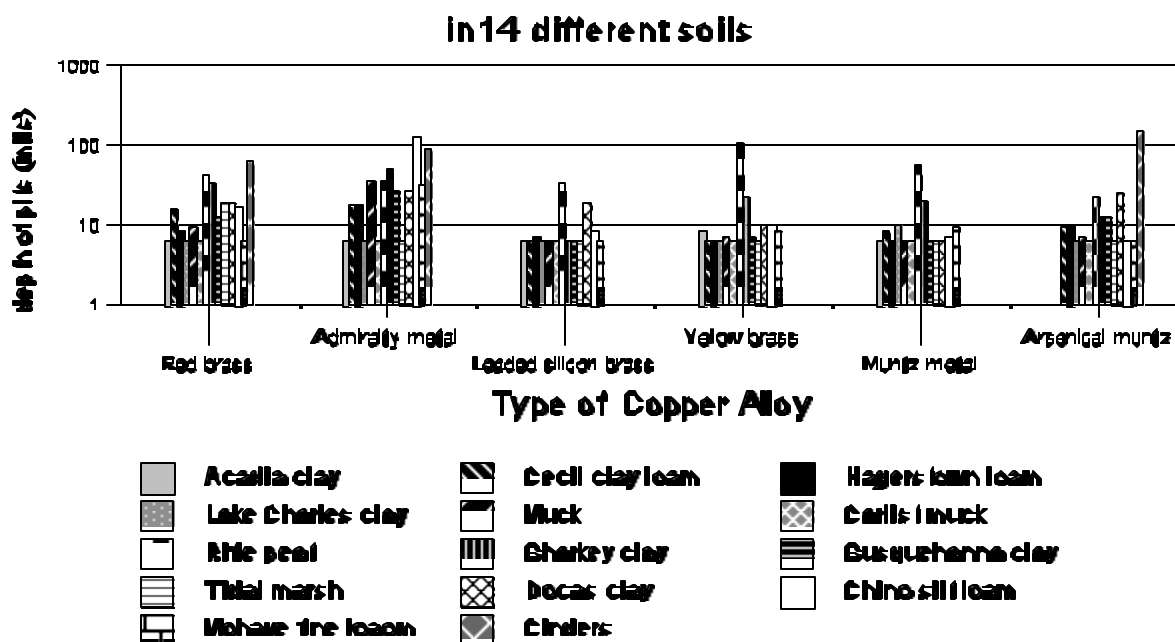
Brasses are basically copper-zinc alloys. The resistance of brasses to corrosion by aqueous solutions does not change markedly as long as the zinc content does not exceed about 15 wt%. Above 15 wt% zinc, there is a great possibility of dezincification occurring. Slowly moving saline solutions, brackish waters, and mildly acidic solutions are environments that often lead to the dezincification of unmodified brasses. Iron and manganese in brass accelerate dezincification, but tin has some inhibiting properties, especially in cast alloys. Arsenic is the only dezincification inhibitor used in aluminum brass. Dezincification takes place slowly in atmospheric exposure and is only a problem when brass is thin, for example fine wires. Industrial and marine atmospheres are more conducive to dezincification than rural atmospheres. Aluminum bronzes are corroded by a type of attack similar to dezincification, which might be called, by analogy, “dealuminification.” Although dezincification is a concern in copper alloys, only a select group of copper alloys are susceptible to this type of corrosion. General corrosion, pitting, and stress corrosion cracking are also predominant corrosion concerns for copper and copper alloys.

In general, brasses and bronzes corrode at about the same rate as copper in industrial, marine, and rural atmospheres. They tarnish to a brown color which eventually turns black, and some finally form a green patina similar to that formed on copper. The high-zinc brasses and the nickel-silvers are more resistant to tarnishing than copper but no tarnish-proof copper alloys have been developed yet.⁽⁶³⁾ Addition of tin significantly increases the corrosion resistance of brasses, especially resistance to dezincification (e.g., Naval brass, which is 60 wt% copper, 39+ wt% zinc, and 0.75 wt% tin). Addition of phosphorus, arsenic, or antimony, typically 0.02 to 0.10 wt%, to brasses effectively produces high resistance to dezincification.

The corrosion rate of brass and bronze in ground waters tends to decrease with time due to the formation of a protective film. However, this layer is brittle and easily cracked permitting continued dissolution of copper ions into solution. The corrosion layer is not truly passivating and corrosion will continue, although at a reduced rate.⁽⁶⁴⁾

Brass pipes or tubes and brass valves and fittings have been used underground for many years. Extensive tests have been made on brass pipes buried in a number of soils for periods up to about 14 years. Chart 4 is a summary of one corrosion study of brass pipes.⁽⁶⁵⁾

Chart 4 - Corrosion of Copper Alloys



The fourteen soils tested are summarized as to pH and location as follows: Acadia clay, pH 6.2, Spindle Top, Texas; Cecil clay loam, pH 4.8, Atlanta, Georgia; Hagerstown loam, pH 5.8, Loch Raven, Maryland; Lake Charles clay, pH 7.1, El Vista, Texas; Muck, pH 4.8, New Orleans, Louisiana; Carlisle muck, pH 5.6, Kalamazoo, Michigan; Rifle peat, pH 2.6, Plymouth, Ohio; Sharkey clay, pH 6.8, New Orleans, Louisiana; Susquehanna clay, pH 4.5, Meridan, Mississippi; Tidal marsh, pH 6.9, Charleston, South Carolina; Docas clay, pH 7.5, Cholame, California; Chino silt loam, pH 8.0, Wilmington, California; Mohave fine gravelly loam, pH 8.0, Phoenix, Arizona; Cinders, pH 7.6, Milwaukee, Wisconsin.

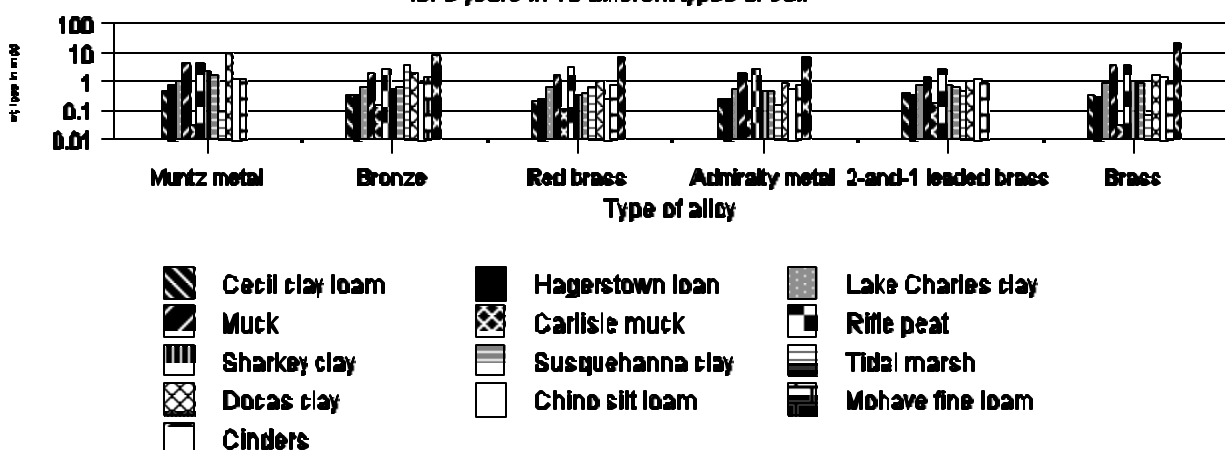
Two soil types produced severe corrosion on all the types of brasses. These soils were Rifle peat (pH 2.6) and Cinders (pH 7.6). In fact three brasses, leaded silicon brass, yellow brass and Muntz metal, were completely destroyed by dezincification in Cinders.

A study by Kirk Logan and Melvin Romanoff ⁽⁶⁶⁾ on copper alloys also showed that most copper alloys corrode much more slowly than stainless steels, which undergo localized pitting, under most, but not all, soil conditions. However, some copper alloys like Muntz metal are unsatisfactory for use in many soils because of destruction by dezincification. Chart 5 shows the corrosion of copper alloys in 13 different soil types for nine years. These data are given as weight loss in mg per square decimeter per day (mdd). The soil types are the same as shown in Chart 4 except that Acadia clay was not used.

This study again showed that Rifle peat and Cinders were very corrosive to copper alloys. In fact, two of the copper alloys, 2-and-1 leaded brass and Muntz metal, were completely destroyed in cinders due to dezincification. Docas clay and muck were also shown to be more corrosive to the copper alloys than most of the other soil types. There are several other studies that were done on these same copper alloys with almost identical results.⁽⁶⁷⁾

Chart 5 - Corrosion of Copper Alloys

for 9 years in 13 different types of soil



The Olin Corporation did a study on the general, localized and stress-corrosion resistance of a series of twenty-one copper alloys in natural atmospheres; of these twelve were either brasses or bronzes.⁽⁶⁸⁾ Three sites were chosen for the study. Site one is New Haven, Connecticut which is characterized as urban-industrial. The rainwater and dew have a low pH and contain sulfates and nitrates typical of industrial atmospheres. In addition it is about two miles from the ocean and a minor amount of chloride is carried to the site by winds as sea salt. Additional chloride contamination from road salt may occur during winter months due to the proximity to several major highways. The site contains only minor levels of ammonia, unlike other industrial environments. Site two is East Alton, Illinois which is classified as an industrial environment. The atmosphere contains particulate matter and corrosive agents. Chloride contamination of this environment is considered to be negligible. The third site, Daytona Beach, Florida, is classified as marine. The environment contains high levels of chloride with negligible industrial pollution. Sea salt spray is carried everywhere by the wind.

Excluding the brasses at high zinc levels ($> 15\%$), the marine environment produced the highest weight losses overall after four years exposure. The corresponding corrosion rate calculations based on weight loss data reveal that, overall, the copper-based alloys were corroding at less than 35.4

um/year [<1 mil per year (mpy)]. This would suggest that the copper oxides formed on all alloys were protective. However, this was not necessarily the case, since many of the alloys suffered from localized corrosion. Table 6 summarizes the results and Table 7 gives the commercial designation and nominal composition for the various brasses and bronzes.

**Table 6. Average weight loss (mg/cm²) for Brasses and Bronzes versus time:
2- and 4-year results at three locations**

Alloy	East Alton 2 years	East Alton 4 Years	New Haven 2 years	New Haven 4 years	Daytona B 2 years	Daytona B 4 years
C22000	2.9	5.0	1.5	3.4	3.1	5.8
C23000	1.8	5.3	1.6	3.7	1.5	2.3
C26000	1.7	5.3	2.2	4.6	0.7	1.2
C42200	1.7	5.2	1.8	4.2	2.4	3.5
C42500	2.7	4.6	1.6	4.0	3.4	6.2
C51000	1.9	4.2	2.1	4.6	6.9	9.7
C51100	3.5	6.2	1.6	3.9	6.8	9.1
C52100	2.1	5.7	1.2	4.8	6.1	12.2
C63800	1.4	4.3	1.4	2.8	2.7	4.7
C66400	2.8	6.2	1.6	5.1	2.6	6.5
C66900	1.8	5.5	2.3	2.9	4.0	7.6
C68800	1.2	4.1	1.2	2.1	0.9	1.9

Looking at the localized corrosion results, the addition of zinc to copper appeared to be detrimental in that selective removal of zinc from the copper matrix was observed to occur in the marine (high chloride) environment even at low zinc levels of $< 15\%$. Dezincification was observed to increase in frequency with increasing zinc levels. In industrial environments, dezincification did not occur until the level of zinc exceeded $15\text{ wt}\%$. Additions of tin to a copper-phosphorus alloy in amounts exceeding $4\text{ wt}\%$ resulted in susceptibility to pitting and crevice attack in the industrial environments. Reduction of zinc to about $10\text{ wt}\%$ and the addition of $1.5\text{ wt}\%$ iron and $0.5\text{ wt}\%$ cobalt eliminated dealloying; however, slight pitting and crevice corrosion susceptibility were still seen in the marine environment. The addition of manganese to a 30% zinc alloy significantly reduces the corrosion resistance. Severe dealloying and stress corrosion cracking were observed in all environments. The silicon bronze alloy

showed some minor dealloying in all environments.

Table 7. Types of Brasses and Bronzes

CDA Designation	Commercial Designation	Nominal Composition
C22000	Commercial bronze	90.0% Cu, 10.0% Zn
C23000	Red brass	85.0% Cu, 15.0% Zn
C26000	Cartridge brass	70.0% Cu, 30.0% Zn
C42200	Lubronze	87.5% Cu, 11.4% Zn, 1.1% Sn
C42500	Lubaloy X	88.0% Cu, 9.3% Zn, 2.2% Sn
C51000	Phosphor bronze	94.8% Cu, 5.0% Sn, 0.2% P
C51100	Phosphor bronze	96.0% Cu, 3.8% Sn, 0.06% P
C52100	Phosphor bronze	91.8% Cu, 8.0% Sn, 0.2% P
C63800	Coronze	95.0% Cu, 2.8% Al, 1.8% Si, 0.4% Co
C66400	Cobron	84.5% Cu, 11.5% Zn, 1.5% Fe, 0.5% Co
C66900	Masiloy	63.5% Cu, 24.5% Zn, 12.0% Mn
C68800	Alcoloy	73.5% Cu, 22.7% Zn, 3.4% al, 0.4% Co

Although all the various copper alloys showed weight loss, the conclusion of the study was that weight loss measurements alone do not reliably predict corrosion performance of copper-based alloys in natural atmospheres. Localized corrosion is more important and should be considered together with weight loss data. Also, the four-year test period was not long enough to predict long-term atmospheric corrosion behavior. Corrosion performance was dependent on both alloy composition and the environment. Industrial environments are much more severe than marine environments in causing stress-corrosion cracking. Only a manganese brass alloy cracked in the marine environment.

The results of a twenty-year study on the corrosion of copper alloys in various atmospheres are shown in Table 8.⁽⁶⁹⁾ This study showed that the industrial and industrial/marine environments were corrosive to all the alloys with the brass (66% copper, 19% zinc, 4% iron, 4% manganese) undergoing the most damage, i.e., corrosion.

Table 8. Corrosion of Copper Alloys in Various Atmospheres - 20 Year Study
Corrosion rate in mpy (mils per year)^a

Metal	Altoona, Pa. Industrial	N.York, N.York Industr- Marine	SandyHk N.Jersey Northern Marine	KeyWest Florida Tropical Marine	LaJolla, Californ. Marine	S.College Pa. NorthernR ural	Phoenix Arizona Dry- Rural
Sn bronze	0.09	0.10		0.03	0.09	0.01	0.01
Bronze	0.06	0.06	0.05	0.01	0.01	0.01	0.01
Brass	0.45	0.35	0.18	0.08	0.08	0.02	0.01
Zn brass	0.07	0.07		0.02	0.01	0.02	0.01
Zn brass	0.12	0.09		0.01	0.01	0.02	0.01
Admiralty brass	0.08	0.10			0.01	0.02	0.01

The specimens were sheet metal, 9" x 12" x 0.035", exposed vertically.

A Swedish study started in 1958 tested 36 copper alloys in sheet or rod form in rural, marine, and urban environments for sixteen years.⁽⁷⁰⁾ The most important effects of atmospheric corrosion on the copper alloy materials were found to be patina formation, general corrosion, and dezincification. During the first years of atmospheric exposure the copper materials acquired a dark coating consisting mainly of cuprous oxide, but also containing basic copper salts, predominantly basic chloride $[\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}]$, which is one of the very few insoluble copper chloride salts, and a basic sulfate $[\text{Cu}(\text{OH})_{1.5}(\text{SO}_4)_{0.25}]$ in the marine atmosphere, basic sulfate in the urban, and basic sulfate and nitrate in the rural atmosphere. The basic carbonate $[\text{CuOH}(\text{CO}_3)_{0.5}]$ occurred only rarely in the rural and urban atmospheres, but the corrosion products formed in the urban atmosphere in many cases contained carbon. The basic copper salts contain the hydroxide (OH) ion in addition to anions, such as chloride, sulfate, or carbonate.

The adhering corrosion products on the copper alloys often consisted of compounds containing alloying constituents: zinc sulfate, in some cases basic zinc sulfate (zinc sulfate that also contains the hydroxide anion similar to basic copper sulfate mentioned above), on some of the brasses, especially in urban and marine atmospheres; lead sulfate, in some cases basic lead sulfate (lead sulfate that also contains the hydroxide anion similar to basic copper sulfate and basic zinc sulfate), on free-cutting phosphor bronze on certain leaded brasses; silica on silicon bronze in the marine atmosphere; copper phosphate on some of the phosphor bronzes containing the higher percentages of phosphorus in the

urban atmosphere; copper arsenate on arsenical copper and on some of the arsenical brasses; nickel sulfate on the nickel silvers in the urban atmosphere.

In the urban and marine atmospheres, signs of green patina appeared on copper after six to seven years and on phosphor bronzes even sooner. The high-zinc brasses did not develop any green patina. In the rural atmosphere no green patina had developed on any material after sixteen years, only various shades of black or brown. The amount of corrosion products retained on the metal surface increased substantially from the seventh to the sixteenth year of exposure. The patina was found to be more protective in the marine and rural atmosphere than in the urban atmosphere.

The average penetration during the whole sixteen-year period was found to be about the same as during the first seven years, but considerably lower than during the initial two years, i.e., rural atmosphere - 0.3 to 0.5 $\mu\text{m}/\text{year}$; marine atmosphere - 0.5 to 0.9 $\mu\text{m}/\text{year}$; urban atmosphere - 0.9 to 1.3 $\mu\text{m}/\text{year}$. The dezincification rate of the brasses had retarded somewhat during the last nine years of exposure.

A similar study on the atmospheric corrosion of copper alloys exposed for fifteen to twenty years was initiated in 1958 by Anaconda Industries on 16 copper alloys.⁽⁷¹⁾ Two marine, one rural, and one urban site were chosen. The results of this study were very similar to the two atmospheric studies mentioned previously.

Charts 6 and 7 show the general corrosion rates for copper and copper alloys in rural, urban, and marine atmospheres for 16 and 20 years and the average corrosion rates for copper alloys during 7 years of atmospheric exposure to rural, industrial, and marine atmospheres.⁽⁷²⁾ These charts show that the urban and industrial atmospheres are the most corrosive to copper alloys while the rural atmosphere is the least corrosive.

An excellent summary of corrosion studies of copper and copper-base alloys in and near water is presented in Chapter 8 of “Corrosion of Metals in Marine Environment - A State of the Art Report.”⁽⁷³⁾ The studies show that depending of the type of copper alloy and the conditions to which it is exposed many of the copper alloys will corrode though generally slower than the stainless steels.

XIII. Bench-Scale Study to Determine the Corrosivity/Leachability of Various Metals from Metal Alloys by The Dragun Corporation for the American Automobile Manufacturers Association (AAMA)

On March 28, 1995 the EPA approved a proposed scope of work/protocol for a bench study to evaluate the corrosivity/leachability of chromium, nickel, and copper from metal alloys, i.e., stainless steels, brass, and bronze, under simulated harsh environmental conditions. This study was in response to an EPA request for additional corrosivity and leachability studies to be conducted on various metals using different sizes in harsh environmental conditions that appeared in the June 29, 1993 Federal Register. This study was conducted by The Dragun Corporation of Farmington Hills, Michigan on behalf of the AAMA.⁽⁷⁴⁾

Three stainless steel alloys (304, 409, and 439) and two grinding fines, aluminum and ferrous obtained from the production process area of an automotive transmission plant, were tested. The compositions of the three stainless steels are found in Table 9 and of the two grinding fines in Table 10. Five different particle sizes (1 cm, 1mm, 100 um, 10 um, and 1 um) were to be tested. The stainless steels were “test blank” rectangular plates from which the five specified average particle sizes were dry-machined. Actual particle sizes used in the study deviated somewhat from the required sizes due to inherent physical/mechanical limitations in the production of the particle sizes from the test blanks. The small mesh particles were prepared by two different methods. One method resulted in sand from the grinding wheel being introduced into the samples which could not be separated; therefore, the amount of alloy tested was actually less than the reported amount.

Table 9. Stainless Steel Chemistry Composition^a

Alloy	% C	% Mn	% P	% S	% Si	% Cr	% Ni	% Ti	% Cu	% Mo
304	0.064	1.40	0.030	0.006	0.48	18.39	8.29	----	0.20	0.17
409	0.005	0.25	0.021	0.001	0.42	11.06	0.15	0.18	0.06	0.03
439	0.005	0.27	0.022	0.003	0.33	17.24	0.22	0.29	0.08	0.06

^a Remainder is iron.

Table 10. Metal Composition of Grinding Fines in mg/kg

Fines	Chromium	Copper	Manganese	Nickel
Aluminum	430	29,000	1,800	670
Ferrous	1,000	not determined	6,100	100

The study was designed to simulate a harsh environmental system in which metal alloys could potentially exist if released to the environment. The conditions used in the study were: an acidic environment, an oxidizing precipitation, a very low permeability soil surface, and a warm and acidic soil. The particles were added at a ratio of 1:10 of metal:rainwater (adjusted to lower pH to represent very acidic soils) and incubated for 6.5 weeks at 55 °C. These incubation parameters were chosen to simulate a one-year incubation in a U.S. surface soil at an average temperature of 77 °F or 25 °C.

Charts 8, 9, 10, and 11 summarize the results of the study, 140 mesh particles are in the range of 107-250 μm , whereas 325 mesh particles are in the range of 46-106 μm .

Chart 8 - Stainless Steel Type 304

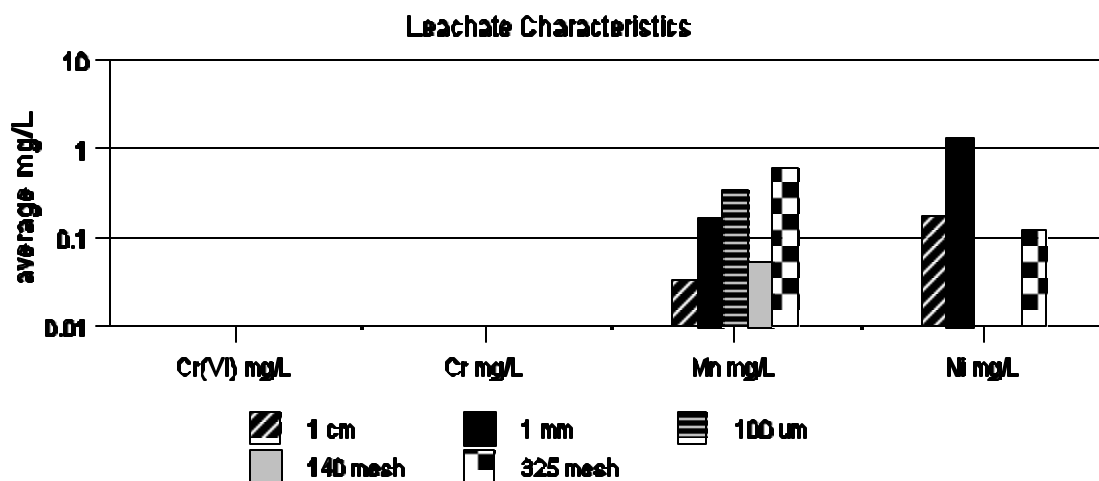


Chart 9 - Stainless Steel Type 409

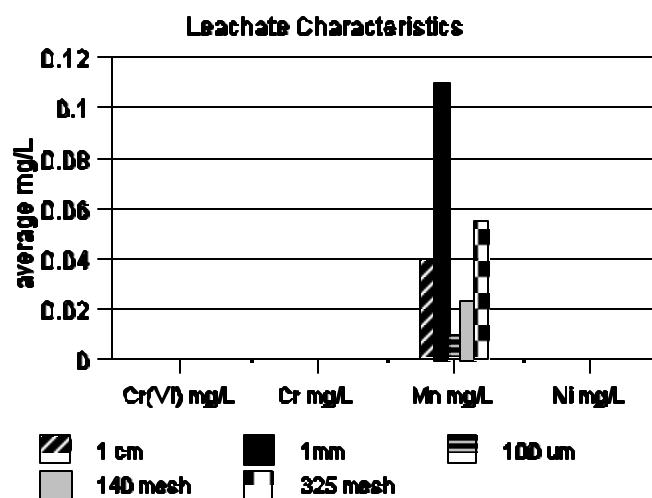


Chart 10 - Stainless Steel Type 439

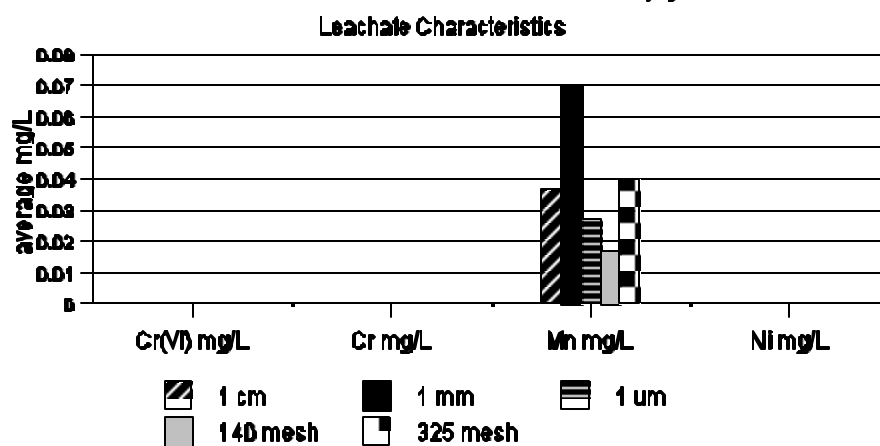
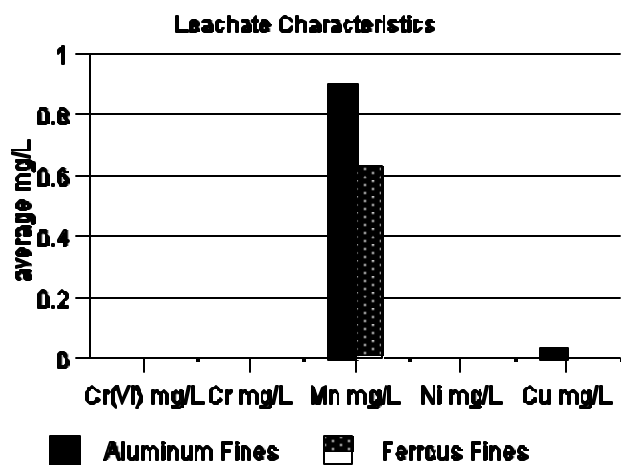


Chart 11 - Aluminum & Ferrous Fines



The above charts indicate that no chromium (VI) or other chromium species were detected in the leachate from any of the five sample alloys tested regardless of the particle size. Therefore, if chromium is leaching from the samples, it is occurring below the detection level of 0.02 mg/L.

Nickel was detected in the 1 cm and 325 mesh samples of 304 stainless steel at levels slightly above the detection limit of 0.01 mg/L. Higher levels of nickel were detected in the 1 mm sample of 304 stainless steel. No satisfactory explanation was given for this anomaly. No nickel was detected above the detection limits in any of the other stainless steels or in the fines. Only the 304 stainless steel contained a high amount of nickel, 8.29%, whereas all the other stainless steels contained < 0.25% nickel. Therefore it seems that nickel will leach above detectable levels from alloys that contain significant amounts of it.

None of the alloys tested contained significant amounts of manganese, smallest 0.18% and largest 1.4%; however, all five alloys tested showed the presence of manganese in the leachate. Stainless steel 304, which contained the highest amount of manganese at 1.4%, also showed the highest amount of manganese in the leachate, varying from 0.03 mg/L (slightly above the level of detection of 0.01 mg/L) in the 1 cm sample to 0.60 mg/L in the 325 mesh sample. There appears to be a relationship between particle size and the amount of manganese in the leachate. Except for the 140 mesh sample, as the particle size was decreased the amount of manganese detected in the leachate increased. The other two stainless steels, which contain < 0.3% manganese, showed concentrations of manganese in the leachate slightly above the level of detection with the highest concentrations occurring in the 1 mm samples. The aluminum fines, 0.18% manganese, and the ferrous fines, 0.61% manganese, had the highest amounts of manganese in the leachate, up to 0.9 mg/L. Therefore it seems that manganese will leach above detectable levels from an alloy even when there is not a significant amount of it present, i.e., < 1%, in the alloy.

Only the leachate from the aluminum fines, 2.9% copper, was analyzed for the presence of copper. Copper was detected at a level of 0.03-0.05 mg/L with a detection level of 0.01 mg/L. The stainless steels contained from 0.06% to 0.2% copper and the ferrous fines contained an average of 0.3% copper but none of the leachates from these samples were analyzed for copper. No brass or bronze alloys were used in the study. The one sample tested showed that copper will leach above detectable levels when present at > 2%.

XIV. Corrosion and Availability of Chromium, Nickel, and Copper

In a recent rulemaking, EPA explained its view of the availability and bioavailability of metals.⁽⁷⁵⁾ The first four paragraphs below summarize some of the information EPA discussed.

Availability of a metal is the extent to which a metal, in either its neutral (M^0) or ionic (M^{+x})

oxidation state, can reach a state of atomic disaggregation. Inorganic metal compounds that are water soluble will dissociate in aqueous media, liberating the metal in its ionic oxidation state. In aqueous solution the metal atoms of the molecules of these substances are disaggregated from the rest of their molecular constituents. In this disaggregated state the metal is available. Water solubility is not a prerequisite, however, for a metal to become available from a metal compound. In the environment a metal can become available from organometallic substances or inorganic metal compounds that are poorly soluble in water, by undergoing environmental transformations that cause the metal atoms to disaggregate and become available. Environmental transformations that cause metals to become available are summarized below.⁷⁵

The extent to which a metal can become available from a metal compound in environmental media is dependent upon: the physicochemical properties of the metal and the metal compound; the structural characteristics of the metal compound; and environmental factors, including, but not limited to: presence of aerobic or anaerobic bacteria, pH, moisture content, and organic matter content of soil or sediments. Some or all of these environmental factors can vary between specific terrestrial or aquatic environments. For different compounds that contain the same metal, the relative availability of the metal from each compound can vary within the same terrestrial or aquatic environment (location). It is also true that the availability of a metal from the *same* metal compound can vary among different terrestrial or aquatic environments. Some metal compounds are more susceptible to environmental transformations and subsequent release of the metal than are other metal compounds.

Bioavailability is the extent to which a substance is absorbed by an organism and distributed to an area(s) within the organism. This is important because the substance can then exert a toxic effect or accumulate. As with availability, the physicochemical and structural characteristics of a substance play an important role in determining whether the substance is bioavailable and the extent to which it is bioavailable. Unlike availability, however, whether a substance is bioavailable and the extent to which it is bioavailable in a given organism also depends upon the anatomy and physiology of the organism, the route of exposure, and the pharmacokinetics of the substance in the organism (*i.e.*, the extent to which the substance is or can be absorbed by the organism from the exposure site, its distribution and metabolism within the organism, and its excretion from the organism). It is important to stress that bioavailability does not by itself mean that a substance is a hazard to human health or the environment. A substance that has 100% bioavailability does not pose a hazard to human health or the environment if it is not intrinsically toxic. Conversely, for substances that are intrinsically toxic it is not necessary for the substance to be 100% bioavailable to cause toxicity. Depending upon the extent of exposure, toxic potency, and the nature of the toxic effect, even substances that have low bioavailability can still pose a hazard to human health or the environment.

An important point to stress regarding the bioavailability of metals is that availability of a metal is not a prerequisite for its bioavailability. Metals can be bioavailable in either their neutral (M^0) or ionic (M^{+x}) oxidation states; or as part of an intact inorganic or organic compound.

Generally the ionic oxidation states of metals are the most available and, for many life forms, the most bioavailable. For aquatic species the bioavailability of a metal is expected to be greater from those metal compounds in which the metal is readily available in aquatic environments than from metal compounds or complexes in which the metal is not readily available in aquatic environments. If the metal is in a completely disaggregated state and dissolved in the aqueous media of the aquatic environment, uptake of the metal by aquatic organisms is favored since they are typically immersed in the aqueous media. However, aquatic species can also absorb intact metal compounds (e.g., organometallic substances). Thus, metals may be bioavailable from metal compounds or metal complexes even where the metal is not available in aquatic environments.

Concentrations of metals in sediments usually exceed those of overlying water by three to five orders of magnitude. With such relatively high concentrations, the availability of even minute fractions of total sediment-associated metal assumes considerable importance. However, the composition of sediments is so complex and variable that it is often difficult, if not almost impossible, to assess the availability of sediment-bound metals.

Some of the most common parameters influencing availability are: (1) pH; (2) oxidation/reduction redox potential; (3) hardness; (4) alkalinity; (5) ionic strength; (6) organic carbon; (7) temperature; (8) inorganic ligands; (9) inorganic oxides of iron, manganese, aluminum and silicon (in sediments only); (10) sulfides; (11) organic chelating agents (e.g., humic substances, organic carbon); (12) concentrations of other metal ions; (13) cation exchange capacity; and (14) methylating agents (for some metals like mercury and arsenic).⁽⁷⁶⁾ These parameters significantly influence the availability of metals in natural waters, sediments, and oil. In water and sediment, the most important of these factors are hardness, alkalinity, pH, oxidation/reduction potential, and the composition of and concentration of ions, particulate matter and organic carbon. Cation exchange capacity can also influence metal availability in soils. For example, the active form of copper, Cu (II), will react with hydroxides and chlorides to form available species, such as cupric hydroxide $[\text{Cu}(\text{OH})_2]$ and cupric chloride $[\text{CuCl}_2]$. Copper may also complex with humic and fulvic acids and clays to become unavailable. A brief discussion of the more important of these factors for the aquatic and terrestrial environments follows.

Aquatic Environment⁽⁷⁷⁾

(1) Water Hardness and Alkalinity

In terms of effects on aquatic life, water hardness is probably the characteristic most studied for its role in governing the toxicity of metals and metal compounds. In general, as hardness increases, toxicity decreases. Hardness is contributed in most natural waters by calcium and magnesium cations. These cations and other similar cations, affect ecotoxicity and availability by competing with metal cations for binding sites and anions. The metals most affected by hardness include cadmium, chromium, copper, silver, and zinc. Because hardness is often correlated with alkalinity and ionic strength, indirect effects such as shifts in buffering capacity or ligand complexations have also been suggested. When

interpreting the effects of hardness, it is important to account for its correlation with other variables such as alkalinity of pH. The effects of such variables should not be confused with an effect of water hardness *per se*. In addition, it is sometimes necessary to consider the separate effects of the different constituents of hardness, rather than their combined effects.

Alkalinity is also known to have a greater influence than hardness on the availability of copper. With copper, water hardness has been found to have no effect under constant alkalinity. While alkalinity has a significant effect on copper toxicity, it has no effect on accumulation of copper in rainbow trout. Alkalinity affects availability in a manner analogous to hardness, but it involves the carbonate anions instead of the calcium and magnesium cations.

(2) Ionic Strength

The ionic strength of surface water will also influence the availability of metals and metal compounds. The high ionic content of salt water, even the dilute salt waters characteristic of estuaries, may compete for uptake with the ionic metal species or may influence the thermodynamic equilibria altering the ratios of metal species in solution.

(3) pH and Redox Potential (Eh)

The pH and Eh of water have a major effect on the physical and chemical forms of metals and metal compounds in an aquatic environment because they control the solubility and concentrations of the major metal species. Increasing the acidity increases the free metal ion concentration in solution due to competition between bound metal ions and free hydrogen ions for the negatively charged exchange sites on organics and inorganics. Under acidic conditions, metals tend to exist in free anionic form, which is believed to impart metal toxicity. The relative and absolute concentrations of the various cations and anions determine which metal species will occur in waters.

(4) Ligands

A major class of chemicals that modify availability is ligands. Ligands are anions or molecules that form coordination compounds or complexes with metals. Ligand influence may be direct, e.g., sequestering the metal by complexation, or indirect, e.g., influencing gill function. Organic ligands play a major role in many aquatic systems. Metals bind to dissolved organic ligands primarily at carboxylic and phenolic functional groups. Organic ligands compete with inorganic ligands and functional groups on biological surfaces for cation binding and consequently influence metal availability.

The five inorganic ligands of primary importance in natural waters, are fluoride, chloride, sulfate,

hydroxyl, and bicarbonate. Also important are carbonate, hydrogen phosphite, ammonia, and in oxygen depleted waters, sulfide and hydrogen sulfide (HS^-) anions. The availabilities of metals are proportional to the hydronium (H_3O^+) ion activity. The hydronium ion is assumed to be the most available form although other complexes may be available.

(5) Suspended Particulate Matter and Organic Carbon

The concentration, size class, and organic carbon content of particulates play a major role in how much of the dissolved metal will complex with solid material and therefore determine the availability of the dissolved metal to aquatic organisms. In addition to the particulate fraction, both dissolved and particulate organic carbon may be important. Metals and metal compounds have an affinity for particulate organic carbon, such that the higher the organic carbon content of suspended particulates, the higher the total concentration of metals or metal compounds. Naturally occurring dissolved organic compounds, such as humic acids, have a substantial effect on the availability of metals and metal compounds.

(6) Interactions at the Sediment/Water Interface

The interface between the sediment and water column, among other factors, represents an important environmental factor governing the fate of metals in an aquatic environment. As particulate matter falls through the water column, metals that are available in the water column may adsorb to the particulate matter and subsequently incorporate into the bottom sediment. (While no longer available, metals that have adsorbed to organic matter may still be bioavailable in aquatic organisms that consume the organic matter.) With time, such surface sediments and their associated metals can become buried. At depth, sediments often become anaerobic as a result of microbial decomposition of organic matter, and the metals may once again become available. For example, under anaerobic conditions iron and manganese are typically reduced to more soluble forms, and become available. Once mobilized, the metal ions migrate upwards as reduced ions through the interstitial porewaters to be reoxidized and fixed in the aerobic surface layer of the sediments. If other metals and metalloids were coprecipitated with the iron and manganese in the sediments and are similarly solubilized under reducing conditions, they will also be subjected to the same mobilization/reprecipitation mechanism. If anaerobic conditions extend above the sediment/water interface, then the potential exists for metals and metalloids to be released into the overlying water column and be available for uptake by aquatic life. It is important to stress that adsorption of metals to organic matter or other matter is not an irreversible process: adsorbed metals can (and often do) become available again, depending upon environmental conditions in the aqueous environment. A more detailed discussion is available.⁷⁵

Terrestrial Environment⁽⁷⁸⁾

Metals may be present in soil in several different forms: as part of the soil parent material or soil minerals of secondary origin; precipitated with other compounds of the soil; sorbed on exchange sites (metal oxides or hydroxide, clay minerals and organic matter can serve as exchangers); either truly dissolved in soil solution, or complexed with inorganic or organic ligands; and embodied in microorganisms, plants, or animals.

The degree of the metals' mobility, activity, and availability is influenced by many factors, particularly pH, oxidation/reduction, cation exchange capacity of the solid phase, competition with other metal ions, and the soil type. Some of the more important properties that influence the fate of metals in the soil are discussed as follows.

(1) Charged Surfaces of Soils

The source and nature of the charge associated with the surfaces of soil particles are important in understanding the fate and subsequent availability and toxicity of soil associated metals and metal compounds. Soil particles, particularly those found within the clay fraction, are commonly electrically charged so that ions in the soil solution are attracted to their surfaces. Both mineral and humic constituents contribute to these electrical charges which arise from different mechanisms of charge generation. Structural, or constant charges, are generated by charge imbalances as a result of substitution or non-ideal occupancy in the clay mineral. pH-dependent charges are associated with reactions of protons at the edges and surfaces of oxide and hydroxide minerals and with certain functional groups of humic substances. The combined organo-mineral colloidal complex plays an important role in controlling the concentration of ions in the soil solution. The retention of metals by soils thus depends upon the degree of acidity or alkalinity of the soil, on its mineralogical composition, and on its organic matter content.

(2) Soil pH

Soil pH plays an important role in controlling the behavior of metals in soils; however, its influence is not as well defined as in the aqueous media because of the heterogeneity of soils, the relatively small proportion of aqueous phase present in soil interstices, and the adsorption of hydrogen ions onto the solid surface. Hydrogen ions are strongly attracted to the surface negative charges and have the ability to replace most other metal cations.

Soil pH is also influenced by changes in the redox potential that can occur as soils become saturated with water. Reducing conditions generally cause pH to increase, while oxidizing conditions tend to decrease pH. Soils have several mechanisms to buffer pH, including hydroxyaluminum ions,

carbon dioxide, carbonates, and cation exchange reactions. Even with these buffering mechanisms, soil pH can vary due to localized conditions within the soil matrix. In general, metals are most mobile under acidic conditions, so that increasing the pH reduces their availability.

(3) Oxides of Iron, Manganese, and Aluminum

The oxides of iron, manganese, and aluminum (the hydrous oxides) have a significant influence on the fate of metals in soils. In freely drained soils, oxides of iron, manganese, and aluminum can co-precipitate and adsorb cations such as chromium, copper, nickel, and zinc, and anions such as hydrogen phosphate and arsenate (AsO_4^{3-}) from solution. Variations in redox conditions affect the quantities of hydrous oxides present in the soils and the adsorptive capacity of a soil for a wide range of cations and anions. Specialized bacteria, such as *Thiobacillus ferrooxidans* and *Metallogenium* spp., are also involved in the precipitation of iron and manganese hydrous oxides, respectively.

(4) Oxidation and Reduction in Soils (Redox)

Redox reactions in soils are frequently slow but are catalyzed by soil microorganisms. If the soils become anaerobic due to water saturation or compaction, anaerobic microorganisms predominate and elements such as manganese, chromium, iron, and copper are gradually reduced. The oxides of iron and manganese can be dissolved either by decreasing pH or redox (Eh); however, the manganese oxides are more readily dissolved than iron oxides. Under such conditions, metals coprecipitated with iron and manganese are released into the soil solution. Under reducing conditions, sulfate ions are reduced to sulfide ions, which can lead to the precipitation of metal sulfides.

(5) Cation Exchange

Positively charged cations in solution are attracted to the negatively charged edges and surfaces of soil particles. If the cations do not form covalent bonds with the surface, then only a weak association is formed between the adsorbed ion and the soil particle. Because of this weak association, the adsorbed ions are easily exchanged by other cations. The cation exchange capacity (CEC) denotes the total sum of exchangeable cations and is commonly expressed as meq/100g of charge per kg soil. Clay, oxides, and organic matter contribute to the CEC of soils. The CEC of the top soil layers that originate from organic matter is much more strongly influenced by pH than the CEC of clay. If cations were adsorbed equally at the surface of charged particles, the ratio of any two cations in solution would be the same as their ratios on the exchange sites. However, there is usually selectivity for cations at the charged surface. This selectivity is attributed to the differences in the valences and hydrated radii of cations at the charged surface. All of these soil properties, each to a different extent, will determine the availability of metals in soils.

Chromium

Chromium occurs naturally in the Earth's crust. Continental dust is the main source of exposure to natural chromium present in the environment. As a result of human activities, however, chromium is released into the environment in larger amounts. Of the estimated 2,900 tons of chromium emitted to the atmosphere annually from anthropogenic sources in the United States, about 35% is in the hexavalent form. Electroplating, leather tanning, and textile industries release large amounts of chromium to surface waters. Disposal of chromium containing commercial products, including stainless steels, and coal ash from electric utilities and other industries are the major sources of chromium released to the soil. Solid waste and slag produced during the roasting and leaching processes of chromate manufacturing, when disposed of improperly in a landfill or when used as fill, can be potential sources of chromium exposure.⁽⁷⁹⁾

Chromium released into the environment from combustion processes and ore processing industries is present mainly as chromium (III) oxide. However, chromium (VI) has been detected in fly ash from coal-fired power plants and from chromate manufacturing and user sites. Chromium is primarily removed from the atmosphere by fallout and precipitation. Most of the chromium in lakes and rivers ultimately will be deposited in the sediments.

On a worldwide basis, the major sources of chromium in the aquatic ecosystems are domestic waste water effluents, metal manufacturing, ocean dumping of sewage, and chemical manufacturing. Chromium in the aquatic phase occurs in the soluble state or as suspended solids adsorbed onto clayish materials, organics, or iron oxides. Most of the soluble chromium is present as chromium (VI) or as soluble chromium (III) complexes and generally accounts for a small percentage of the total. Soluble chromium (VI) may persist in some bodies of water for extended periods, but eventually will be reduced to chromium (III) by organic matter or other reducing agents in water.

In 1988 the release of chromium to soil amounted to about 82.3% of the total environmental release from manufacturing and processing facilities in the United States. On a worldwide basis, the disposal of commercial products containing chromium, which includes stainless steels, may be the largest contributor of chromium releases to the soil, accounting for about 51% of the total. Chromium (III) in soil is mostly present as insoluble carbonates and oxides and therefore will not be mobile in soil. The sorption of chromium to soil depends primarily on the clay content of the soil, and to a lesser extent, on ferric oxide and the organic content of the soil. The solubility of chromium (III) in soil and its mobility may increase due to the formation of soluble complexes with organic matters in the soil. A lower soil pH may facilitate complexation.⁽⁸⁰⁾

Chromium (III) and chromium (VI) are readily interconvertible under natural water conditions. The reduction of chromium (VI) by sulfide or ferrous (Fe^{+2}) ions under anaerobic conditions is fast, whereas the oxidation of chromium (III) is quite slow. Chromium speciation in groundwater depends on the redox potential and pH conditions in the aquifer. Chromium (VI) predominates under high oxidation conditions, whereas chromium (III) predominates under reducing conditions. Oxidizing

conditions are generally found in shallow aquifers, and reducing conditions generally exist in deeper groundwaters. In seawater chromium (VI) is generally stable. The speciation of chromium in natural groundwater also depends on pH. In natural groundwater the pH is typically 6-8 and CrO_4^{2-} , the chromium (VI) species predominates. The dominant chromium (III) species in groundwater at pH 6-8 is $\text{Cr}(\text{OH})_2^{+1}$. This species and other chromium (III) species will predominate in more acidic pH, whereas $\text{Cr}(\text{OH})_3$ and $\text{Cr}(\text{OH})_4^{-1}$ predominate in more alkaline waters.⁽⁸¹⁾

The fate of chromium in soil is dependent, in part, on the redox potential and the pH of the soil. In most soils chromium will be present predominantly in the chromium (III) state. In deeper soil where anaerobic conditions exist, chromium (VI) will be reduced to chromium (III) by the sulfide and ferrous ions present in the soil. The reduction of chromium (VI) to chromium (III) is facilitated by low pH. Chromium (VI) is reduced by iron (II), dissolved sulfides, and certain organic compounds with sulfhydryl groups, while chromium (III) is oxidized by an excess of manganese dioxide. In general, chromium (III) is considered to be the stable form in soils; however, oxidation to chromium (VI) can occur readily under conditions prevalent in many field soils. The oxidation of chromium (III) to chromium (VI) in soil is facilitated by the presence of low oxidizable organic substances, oxygen, manganese dioxide, and moisture. Oxidation is also enhanced at elevated temperatures in surface soil that result from brush fires. Organic forms of chromium (III) (e.g., humic acid complexes) are more easily oxidized than insoluble oxides. Reduction of chromium (VI) compounds and oxidation of chromium (III) compounds in soils may occur simultaneously.⁽⁸²⁾

It has been shown that water treatment involving chlorination will effectively transform chromium (III) to chromium (VI). The normal presence of residual oxidizing capacity in treated water is capable of maintaining dissolved chromium in the higher valence (VI) state. If chromium (III) is present in high concentrations in well water, chlorination of the well water can result in correspondingly high concentrations of chromium (VI) in the water.⁽⁸³⁾

Nickel

Nickel and its compounds are naturally present in the earth's crust and releases to the atmosphere occur from natural discharges such as windblown dust and volcanic eruptions, as well as from anthropogenic activities. The major anthropogenic sources of nickel are the burning of fuel oil, nickel metal refining, steel production, nickel alloy production, and coal combustion.

While nickel forms strong, soluble complexes with hydroxyl, sulfate and bicarbonate anions, in aerobic waters at environmental pHs (< 9), the predominate form of nickel is the hexahydrate $[\text{Ni}(\text{H}_2\text{O})_6^{2+}]$ ion. Complexes with naturally occurring anions, such as hydroxyl, sulfate, and chloride are formed only to a small degree. Complexes with hydroxyl radicals are more stable than those with sulfate, which in turn are more stable than those with chloride. Nickel (II) hydroxide becomes the dominant species above pH 9.5. In anaerobic systems, insoluble nickel sulfide forms if sulfur is present, thus limiting the availability of nickel. In soil, the most important sinks for nickel, other than soil

minerals, are amorphous oxides of iron and manganese. The mobility of nickel in soil is site specific with pH being the primary factor affecting leachability. Mobility increases at low pH.⁽⁸⁴⁾

Nickel is strongly adsorbed to soil, although to a lesser degree than lead, copper, and zinc. Soil properties such as texture, bulk density, pH, organic matter, the type and amount of clay minerals, and certain hydroxides influence the retention and release of metals by soil. Amorphous oxides of iron and manganese, and to a lesser extent clay minerals, are the most important adsorbents in soil. In alkaline soil adsorption may be irreversible, which would limit the availability and mobility of nickel in these soils. Cations, such as calcium and magnesium, reduce adsorption of nickel due to their competition for the binding sites, whereas anions like sulfate reduce adsorption as a result of complexations with the nickel ion. The presence of complexing agents, such as EDTA (ethylenediamine tetraacetic acid), dramatically lowers nickel adsorption, which has important implications at waste disposal sites if chelating agents are also present.⁽⁸⁵⁾

Copper

Copper and its compounds are naturally present in the earth's crust. In general, most copper in soil is in mineral form or tightly bound to organic matter. Copper will adsorb to organic matter, carbonate minerals, clay minerals, or hydrous iron and manganese oxides. Sandy soils with low pH have the greatest potential for leaching. In most temperate soils, the pH, organic matter, and ionic strength of the soil solutions are the key factors affecting adsorption. The ionic strength and pH of the soil solution affect the surface charge of soils and therefore influence ionic interaction. When the amount of organic matter is low, the mineral content of iron, manganese, or aluminum oxides becomes important in determining the adsorption of copper. Copper binds to soil much more strongly than other divalent cations and the distribution of copper in the soil solution is less affected by pH than are other metals. If the organic matter in soil is removed there is a dramatic reduction in adsorptivity of the copper, which demonstrates the importance of organic matter in binding copper. Copper is much more soluble in an oxidizing environment. In a reducing environment, solubility is low, possibly due to the formation of insoluble sulfides.⁽⁸⁶⁾

The median concentration of copper in natural water is 4-10 ppb. It is predominantly in the Cu (II) state. Most of it is complexed or tightly bound to organic matter, little is present in the free or hydrated form. Organics (humic substances) and iron oxides are the most important contributors to the binding of copper by aerobic sediments. In anaerobic sediment, Cu (II) will be reduced to Cu (I) and insoluble cuprous salts will be formed. In general the Cu (I) ion is unstable in aqueous solution, tending to disproportionate to Cu (II) ion and copper metal unless a stabilizing ligand is present. The only cuprous compounds stable in water are the insoluble ones such as cuprous sulfide, cuprous cyanide, and cuprous fluoride. In the Cu (II) state copper forms coordination compounds or complexes with both inorganic and organic ligands. Ammonia and chloride ions are examples of species that form stable ligands with copper. Copper also forms stable complexes with organic ligands, such as humic acids.⁽⁸⁷⁾

Natural waters contain varying amounts of inorganic and organic species affecting the complexing and binding capacity of the water and the types of complexes formed. In seawater, organic matter is generally the most important complexing agent.

The major species of soluble copper found in freshwater or seawater over a range of pHs are Cu^{+2} , $\text{Cu}(\text{HCO}_3)^+$, and $\text{Cu}(\text{OH})_2$. At the pH values and carbonate concentrations characteristic of natural waters, most dissolved Cu(II) exists as carbonate complexes rather than as free or hydrated Cu (II) ions. The most significant precipitate formed in natural waters is malachite $[\text{Cu}_2(\text{OH})_2\text{CO}_3]$. In anaerobic waters, cupric sulfide, cupric oxide, and metallic copper form and settle out. The combined processes of complexation, adsorption, and precipitation control the level of free Cu (II) ion.⁽⁸⁸⁾

XV. General Summary of Peer Review Comments

This document was peer reviewed by five reviewers, Robert Baboian, Ph.D., P.E.,⁽⁸⁹⁾ C. Paul Dillon, P.E.,⁽⁹⁰⁾ Russel D. Kane, Ph.D.,⁽⁹¹⁾ Susan R. Freeman, P.E.,⁽⁹²⁾ and Prof. Florian Mansfield.⁽⁹³⁾ Changes were made to the document based on their comments. Additional comments and/or observations are discussed below.

Most of the peer reviewers agree that corrosion rates for large pieces of alloys can be extrapolated to smaller pieces as long as the dimensions of the pieces do not change drastically. However, extrapolation to very small pieces or fine particles is generally not valid because the large increase in surface area can cause the corrosion rates to increase even by orders of magnitude.

The general consensus from the peer reviewers is formation of passive films and true oxide layers or barriers on the alloys is not dependent on the size or overall shape of the sample. Other factors, such as: sample geometry (in as much as crevices and crevice conformations are formed); electrolyte chemistry; and galvanic coupling influence the formation and affectivity of the barriers. The structures and compositions of the films or barrier layers are dependent primarily on the composition of the alloys themselves.

All of the peer reviewers contend that the “harsh environment” used by The Dragun Corporation in their bench study does not represent typical conditions in the actual environment. Several important factors were missing in the “harsh environment” that contribute greatly to the corrosion of alloys in the field. These include the presence of chloride, sulfur, and other chemical species, as well as microbes and/or bacteria.

The peer reviewers had several major concerns about the results of the study conducted by the Dragun Corporation. These concerns include the following:

- (1) Enough time may not have elapsed for the metals to have shown up in the leachates;
- (2) Re-deposition of corrosion products on the surface of the metal may be responsible for the lack of the metals in the leachates;
- (3) Only one of the samples contained a significant amount of nickel and that was the one sample which had nickel in the leachate. The lack of nickel in the other leachates reflects the lack of nickel in the alloys themselves;
- (4) In the aluminum fines experiment the reason that more copper did not show up in the leachate was due to the fact that the copper in the alloy dissolves, then re-deposits as an oxide on the aluminum surface. Therefore, most of the dissolved copper remains on the alloy surface and cannot be detected in the leachate even though it has leached out of the alloy;
- (5) The variation in the surface color of the various fines used indicates a variation in the surface film characteristic which can produce differences in the corrosion behavior of the alloys;
- (6) There is serious doubt that the acceleration factor of 6.5 weeks for testing represents 52 weeks in southern soil, is correct. Thermodynamics predicts a doubling of the reaction rate with each 10 °C rise in temperature. However, when protective films on alloys are involved, kinetics become important and therefore, the doubling estimate is not necessarily valid. Since passive films are very important in the corrosion rate of the materials in the study, the calculated acceleration is probably not accurate. In addition, packing of the alloy particles introduces a crevice configuration which enhances localized corrosion, such as pitting and crevice corrosion. The affect of temperature on localized corrosion is therefore quite complex with the alloys. An even more complex situation occurs due to the disturbing of the packed alloy particles by agitation twice a week. If the induction period for localized corrosion is shorter than the 3.5 days between agitations, then this localized type of corrosion will initiate during the period between agitations. If the induction period is longer than 3.5 days, then agitation will inhibit localized corrosion. In the packed configuration, oxygen depletion can occur, thus reducing the corrosion rate with time. However, agitation insures that reducible species, such as oxygen, are not permanently depleted at the surface of the packed alloy particles;
- (7) The solubility of the corrosion products will affect the results. Thus, the corrosion rate of the alloy may be high, but if the corrosion products are insoluble in the electrolyte, then the products will build up on the sample surface and will not be found in the electrolyte.

XVI. Conclusions

Corrosion studies that have been reviewed for both stainless steel and the copper alloys, brass and bronze, show that all stainless steels and all types of brass and bronze will corrode, at least to some extent. Some stainless steels, e.g., the 300 series, and certain types of brass and bronze corrode very slowly in certain types of soils and under certain conditions, while other types of stainless steels, e.g., the 400 series, and some brass and bronze corrode fairly rapidly and can be completely destroyed in less than 15 years in certain types of soils and under certain types of conditions.

The corrosion studies also showed that for the more corrosion resistant stainless steels the corrosion rate decreases with time due to the formation of a protective layer on the surface of the alloy. This protective layer adds to the corrosion resistance of the alloy. The layer, however, can be broken by abrasion or chemicals resulting in an increase in corrosion rate until the layer is reformed on the surface. The less corrosion resistant stainless steel alloys also showed a decrease in corrosion rate; however, this was mainly due to either the complete destruction of the alloy or to holes and/or perforations occurring in the alloy.

In the corrosion studies on the copper alloys, brass and bronze, the corrosion rates were also observed to decrease slightly with time. The decrease in rate is due to the formation of a protective layer on the surface of the alloy. Like stainless steel, this protective layer can be broken, resulting in an increase in the corrosion rate until the layer is reformed. Overall, the corrosion rates of copper alloys are lower than the corrosion rates of some stainless steels.

The studies reviewed were generally done on flat pieces of metal or on pipes/tubes, but for most studies no actual dimensions were given. With the exception of the AAMA study, no corrosion studies were found that used very small pieces of the alloys, i.e., small particles, shavings, turnings, etc. However, if large pieces of the alloys were found to corrode substantially under certain conditions, then small pieces of the same alloys may be expected to corrode considerably faster. Extreme care must be taken when extrapolating corrosion rate data for an exposed strip of alloy material to corrosion rates for small pieces of alloy. The small pieces of alloys generally are packed and include crevice configurations. Overall, crevice corrosion rates for alloys are much higher than uniform corrosion rates and therefore higher corrosion rates would be expected for the packed configuration. However, with the packed configuration a percentage of the surface area may be shielded from the electrolyte or be affected by stationary electrolyte depletion of reducible species. Examples are depletion of oxygen and/or hydrogen ions. Under these circumstances, a lower corrosion rate would occur.

The magnitude of the affect of alloy exposure configuration is dependent on a number of factors. First is the differences in atmospheric, immersion, and soil burial exposures. The soil burial environment is an in-situ stationary electrolyte. Therefore, the effect of the alloy packing configuration in soils may be minimized. However, the effect of alloy surface shielding, due to packing, may be significant. Both crevice geometry and shielding are important for atmospheric and immersion

exposures. Second, the nature of the alloy is important. Active-passive alloys, such as stainless steels, are highly susceptible to crevice corrosion. Therefore, geometries which include multiple crevices will enhance the crevice corrosion mechanism with these alloys. A third factor is the chemistry of the environment. For many alloys, severe crevice corrosion occurs in chloride-containing environments. Thus, when chlorides are present in the environment, crevice corrosion due to alloy packing can be significant.

The bench study conducted by The Dragun Corporation in 1996 for the AAMA did not show consistent trends in the data. The small mesh particles were prepared by two different methods. One method resulted in sand from the grinding wheel being introduced into the samples which could not be separated; therefore, the amount of alloy tested was actually less than the reported amount. The amount of metal ion released into the water was not determined quantitatively. Chromium was not detected in any of the leachates in the study conducted by the Dragun Corporation. In the same set of experiments it was observed that nickel, copper, and manganese leached out of the alloys above the level of detection. In addition, the test results did not show a direct relationship of increasing corrosion with decreasing particle size, except for the manganese in the 304 stainless steel sample. The electrolyte solution used in the bench study done by The Dragun Corporation did not represent a real world corrosive electrolyte. Such an electrolyte would contain chloride ion and/or significant sulfur compounds beyond the small amount of sulfuric acid used for pH adjustment.

No evidence of interest in or experimental work being done on the fate/corrosion of small particles of alloys in environmental situations was found. The bench study submitted by the AAMA did not provide an adequate basis for a particle size exemption. No information was found on the fate/corrosion of the alloys in landfills.

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