Corrosion Prevention and Control:

A Program Management Guide for Selecting Materials

Spiral 2

AMMTIAC

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for Selecting Materials

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Advanced Materials, Manufacturing, and Testing
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Preface

This handbook was produced by the Advanced Materials, Manufacturing, and Testing Information Analysis Center (AMMTIAC), and presents a metallic materials selection guide for program managers to reduce the effects of corrosion and decrease life-cycle costs. This handbook represents the second edition of a corrosion handbook first published in July 2005 by AMMTIAC's immediate predecessor; the Advanced Materials and Processes Technology Information Analysis Center (AMPTIAC).

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AMMTIAC is a full-service DoD Information Analysis Center and is well oriented to the needs of its user community. It searches, identifies, collects, reviews, analyzes, appraises, summarizes, computerizes, stores, and provides timely information and data; and advisory, analysis, and other services concerning the available worldwide scientific and technical information and engineering data on ceramic and several other materials that are important to the DoD.

In the area of metals, AMMTIAC serves as the DoD's central source of engineering and technical data and research and development information on monolithic metals, metal reinforced composites and metal matrix composites, honeycomb structures, hybrids, and laminates. Emphasis is placed on metals used in critical structural and non-structural components in military systems. Such applications include vehicle components including skins, engine components, drive/control components, electronics and electrical systems, armors, and structural components. Additional applications include weapon components, ammunition, and immobile structures.

AMMTIAC's library holds information covering such subject areas as metal properties (especially mechanical properties as a function of composite architecture, temperature, and environmental conditions); latest research and development concepts, results, and trends; application and processing of metals; processing equipment; measurement and testing of metals; test methods; quality control related to metals; corrosion/deterioration detection, prevention and control, and other environmental effects on metals and systems; producers, suppliers, and specifications for metals of concern to the DoD. Properties for other materials, such as ceramics, organics and their composites are covered by AMMTIAC in a similar fashion.

Further questions about this report and other AMMTIAC products and services should be directed to the following: AMMTIAC, 201 Mill Street, Rome, NY 13440-6916. AMMTIAC may also be reached at (315) 339-7117, Fax: (315) 339-7107 or by visiting the AMMTIAC site on the World Wide Web (WWW) at URL: http://iac.dtic.mil/AMMTIAC.

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1.0 Reducing Acquisition Risk By "Designing In" Corrosion Resistance

Corrosion is a process that occurs when a material deteriorates due to its interaction with the surrounding environment in which an electrochemical reaction consumes the material through oxidation. As a material corrosively deteriorates, its material properties likewise degrade. The result of corrosion manifests itself as weapon system or component failure at the worst or unsightly appearance at the best (Figure 1), and it's important to realize that corrosion occurs in nearly all weapon systems and operating environments. Corrosion can significantly impact readiness of DOD systems if excessive maintenance is required to ensure continued safe operation. Corrosion costs can be extensive and for complex systems combating its effects can take a great deal of time and expertise to correct. Overall, the costs of combating corrosion are very high. A recent, federally funded study has estimated the cost to the DOD at over $20B per year.[1]

Figure 1   Corrosion of a Military Ground Vehicle

Unfortunately, it is often the case that systems are designed to meet performance goals where strength, weight, thermal, and electrical requirements are primary technology considerations while other important attributes such as corrosion resistance and environmental compatibility receive far less attention. Without an upfront analysis to mitigate corrosion, problems often occur after the system has been implemented into service. Correcting unanticipated corrosion during the operational phase of the lifecycle can be very costly. In some cases it may be impossible to return the system to its original state without replacing problematic components or structures at great expense.

Developing new systems that are inherently corrosion resistant, either through the selection and use of corrosion resistant materials or, if appropriate, by employing corrosion preventative compounds and coatings, is one sure way to reduce total ownership costs. However, these considerations must be made early in the acquisition cycle to be effective. Design and acquisition management practices must recognize corrosion as a risk factor to be managed.

Corrosion resistance is one factor that dictates how the system will perform over the long haul, but unlike other performance issues it is difficult to quantify. Intuitively one knows that combating corrosion, especially if it is unplanned, can and will influence a variety of factors including reliability and total ownership costs. Improving acquisition practices to ensure that corrosion resistance is designed in 'up front' is the only sure way to field a system that will have the readiness, mission availability rates, and ownership costs that sustain themselves at predictable values. This is especially important as the design life of weapon systems continues to climb.

If one recognizes that corrosion is an acquisition risk factor to be managed, then the question becomes: what design practices are used to ensure that a system possesses the desired corrosion resistance? *Materials selection* is the process used by designers to choose a material that meets the various performance attributes required by the system design specifications while also considering other factors such as cost and appearance. To ensure adequate maintainability, predictable corrosion resistance should be accounted for during design.

Due to various factors including available time and training deficiencies, designers often overlook tasks needed to ensure adequate corrosion resistance. To be totally effective, designers must consider the inherent corrosion resistance of the selected structural materials in the environment they will operate in, any potential interaction these materials may have with adjacent materials, design details that may exacerbate corrosion problems, and the corrosion prevention technologies such as coatings and other compounds needed to minimize maintenance requirements. If little thought is given up-front to select the best combination of structural materials and corrosion prevention technologies, then a maintenance nightmare may be in the making!

Ensuring that a system will age gracefully must involve all of the stakeholders in the development process including the design activity, as well as the DOD program manager and their staff. Corrosion is a risk factor that if managed improperly can result in a system that is far more expensive to maintain than desired. Mitigating corrosion-induced reliability and maintenance problems most certainly will affect readiness and operations and maintenance (O&M) budgets. If the DOD acquisition program office and the prime contractor work together and consider corrosion prevention and control early in the development cycle, then total ownership costs can be reduced from the onset. The discussion here has focused entirely on corrosion of weapon systems but the topic equally applies to support equipment as well as infrastructure such as buildings, tanks, underground piping, and the like.

1.1 Reducing Acquisition Risk and Total Ownership Cost

As mentioned previously, the best way to prevent or minimize corrosion throughout a system's lifecycle is to consider corrosion tolerant materials and corrosion prevention and control technologies when selecting materials during the design process. This is essential to preserve a system in its original corrosion resistant state after it has been introduced into service. Although enhancing the materials selection process to pay closer attention to corrosion prevention and control may cost more initially, there are many potential benefits that will result including improved reliability, reduced maintenance, increased availability, improved performance and efficiency, improved safety, increased service life, and reduced life-cycle cost. In addition,

extending the life of a fielded system is far easier and less costly if excessive corrosion is prevented from occurring in the first place.

1.1.1 System Life Cycle

Figure 2 illustrates the life cycle of a system as it relates to component failure. Known as the 'bath tub curve', the figure demonstrates the various rates at which components may fail during its service life. Generally this figure addresses the sum total of all failures, including those induced by corrosion. However, it's reasonable to assume that a similar curve would result from failures due to corrosion alone.

As illustrated on the curve, the three phases of a system life cycle consist of 1) introduction of the system into service, 2) normal operational use and 3) wear-out. During the introductory phase the manufacturing defects are identified and corrected, which results in a higher number of failures initially, followed by a steady decline. For systems designed with inappropriate attention to corrosion, this initial phase corresponds to the identification and mitigation of unexpected corrosion. The bulk of the life cycle is spent as the system operates normally (the second phase) with only routine maintenance and repairs. It is very important to properly maintain the system during this phase by employing corrosion preventative measures. If steps are not taken, the system will corrode, thus accelerating the initiation of the third phase where the number of failures and associated maintenance actions, including component replacement, begins to increase steadily as the system reaches its maximum operational life. Proper materials selection during the design phase, followed by the use of appropriate corrosion prevention and control practices during service, will delay the onset of wear-out and enable the affordable extension of a system's life.

In direct correlation to the number of failures shown in Figure 2 is the total ownership cost. As the amount of failures and extraordinary corrosion preventative measures rise, so does the total cost. In a system that has not been designed with inherent corrosion resistance, it can be expected that the wear-out phase will be reached in a shorter period of time. Consequently, an entirely new system would have to be purchased or alternatively, extensive maintenance would be necessary to keep the existing system in operation, which would carry significant costs.

While it's difficult to definitively project a return on investment that would result from increased attention to corrosion prevention and control during system design, intuitively it is quite easy to understand that a system designed with inherent corrosion resistance will last longer than one without. Figure 2 addresses both situations, with the dashed lines indicating a longer service life for the system designed with corrosion resistance in mind. Take for example a hypothetical weapon system that, due to its inherent corrosion resistance, has a life span that is two years longer than a similar (baseline) system. If the baseline life was ten years and the total acquisition cost were $1B, the return on investment due to delayed acquisition of a follow-on system would be $200M. In reality the cost savings would be higher than this projection because this example totally ignores operations and maintenance savings. Mitigating unexpected corrosion can be very expensive, both in terms of direct cost but also impacts to readiness. If a system were designed with corrosion resistance built-in, then less maintenance would be required, thus saving O&M funding while at the same time increasing system availability. It can be easily seen that extending the service life of a system before it reaches the wear-out phase is extremely beneficial

in terms of cost avoidance and that the savings can be extremely high, especially if the acquisition of a new system is delayed.
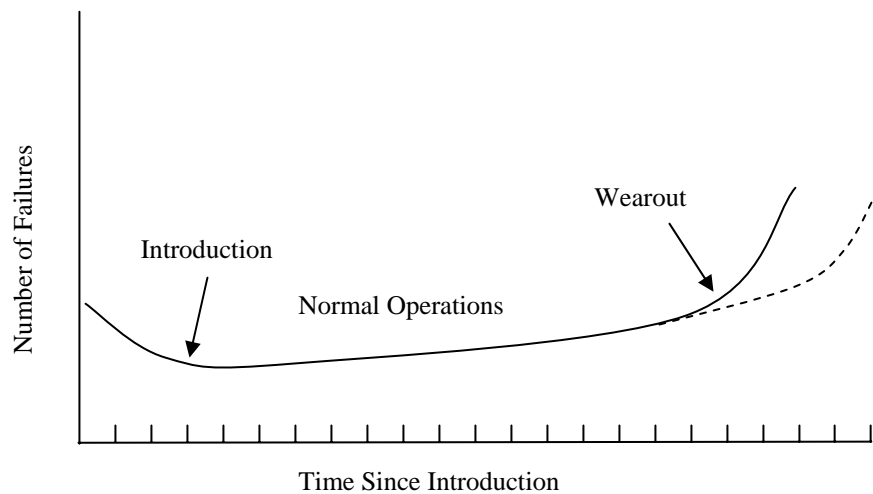
Figure 2   Classic System Life Cycle

Another way of considering the influence that corrosion prevention and control has on total ownership costs is displayed in Figure 3. This figure depicts the acquisition costs versus time for two hypothetical systems, one designed with inherent corrosion resistance and the other without. As shown on the figure, the acquisition costs for the system designed to possess enhanced corrosion resistance will be higher due to increased engineering time and potentially more expensive materials. However, over the life of the system these costs will be recovered do to O&M cost savings, so that the total ownership costs of the corrosion resistant system will be lower than the baseline system.
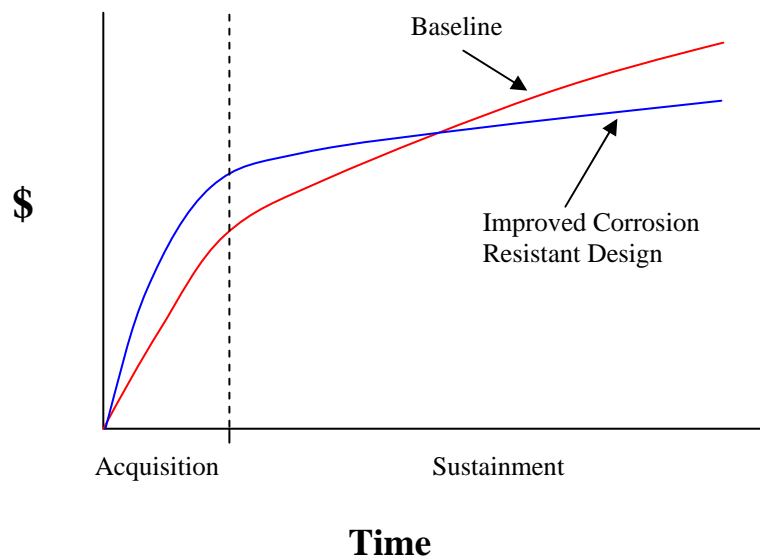
Figure 3   Total Ownership Cost Comparison

1.1.2   Managing the Risk Factor

If one accepts the premise that corrosion is a risk factor, that if poorly managed it will increase total ownership costs, then one might ask: how do you manage the risk? Developing a new system with the lowest total ownership cost can only be done if proper oversight and attention is paid to material selection during the design process. At the moment there are no available management tools that can calculate the return on investment that would result from increased attention to corrosion prevention and control during the design phase. Intuitively it is obvious that if corrosion is controlled, then readiness will increase through increased availability and reliability coupled with decreased maintenance. The challenge for a program manager and the prime contractor is accounting for the risk of corrosion so that these benefits can be realized while minimizing total ownership costs.

Similar to the absence of existing management tools to predict the reduction of total ownership costs due to improved corrosion prevention and control, there is also a lack of a formal procurement process to account for corrosion prevention and control. Prior to the implementation of the Acquisition Reform Initiative, military specifications and standards codified the lessons learned from observations of failures and correctable problems on legacy systems. These lessons learned included substantial information on corrosion prevention and control. When the majority of these documents were rescinded in the early 1990's, the increased risk of corrosion and the associated impact on readiness and total ownership cost was not considered. Similar to other risk-related activities such as survivability, manufacturing, and reliability, corrosion prevention and control would tremendously benefit if a risk analysis were conducted during the system engineering process. Accounting for and managing the risk associated with corrosion prevention and control will undoubtedly reduce ownership costs.

1.2   Materials Selection to Ensure Corrosion Resistance

The successful consideration of corrosion prevention and control during the materials selection phase of the design process is key to developing systems that will age in a predictable and affordable fashion. It should be noted that the process of materials selection is not used solely to choose the material to build a structure or component. Rather, it is used to select a system of materials that together provide the necessary mechanical, thermal, electrical, and physical properties needed to meet performance requirements while simultaneously providing the necessary resistance to environmental attack including corrosion.

Materials selection is a crucial part of the design process; however it is a process that can lead to future problems, especially if the designer focuses upon meeting performance requirements while giving little thought to maintenance needs. As mentioned above, it's imperative that designers consider the requirements for corrosion prevention and control (CP&C) early on. The use of CP&C methods must be planned and not an afterthought, or else the probability that maintenance problems will plague the system throughout its service life will be high. CP&C methods include an array of technologies such as chemical treatments, paints, platings, and cathodic protection to name a few.

1.2.1   Impact of the Corrosive Environment

Planning for the graceful aging of a structure or system during materials selection requires a firm understanding of the environment it will be operating in. The word environment used here

describes the conditions a system may be exposed to while in service. For example, a ship floating in the ocean is thought to be in a marine environment. Another example is the high temperature environment turbine blades experience inside a jet engine during operation. In reality though, things are not quite that simple because systems experience a variety of simultaneous environmental conditions. Systems often contain many fluids and chemicals that are necessary for its components to operate, but some of these can be very corrosive and cause a material to degrade. For instance, designers must consider cleaning chemicals and hydraulic fluids as sources of contamination that can cause a material to corrode. There are many other materials and contaminants that exist within the operational environment that can influence the rate at which a structure or component corrodes. Designers must take a step back and gain a firm understanding of all environmental factors that can influence corrosion before selecting the construction materials. Again, it's important to note that the 'environment' as is described here isn't a single condition but rather a combination of factors, which work in concert, such as operating temperature and humidity, salinity, and mechanical loading. Other contributing influences include chemicals, fuel, and pollutants to name a few.

Having a firm understanding of the operational environment is crucial to designing a corrosion resistant system. However there are other environmental conditions that occur during storage or transportation that must also be considered. As Figure 4 attests, systems can experience corrosive environments during transportation that are far more severe than their operational conditions, yet designers can easily overlook the threat of transportation induced corrosion since systems experience only brief periods being transported from one part of the globe to another. Storage conditions must also be analyzed to determine whether they may damage or degrade a system. Some weapons like air-launched missiles are stored in controlled humidity containers, which helps keep the system in its pristine, uncorroded state. Other weapons, like the gravity bombs shown in Figure 5, may experience extremely high humidity levels while in their protective shelters. As shown in this figure, these weapons can experience severe corrosion, so much so that they may become useless and have to be replaced at a significant cost.

1.2.2 The Importance of Corrosion Testing and Information Resources

One of the reasons why the selection of corrosion resistant materials is a challenging process is that corrosion data isn't usually available in a form that is immediately and directly related to the environment that the system or structure will be subjected to. Because of the extremely large number of materials, including variants subjected to different fabrication processes, and environmental conditions, it is too costly and nearly impossible to test all the combinations of material and environment. The result is that it can be very difficult to find completely relevant data that substantiates a decision. Materials scientists over the years have devoted significant resources to corrosion testing and analysis. Accelerated testing using salt spray or controlled humidity and temperature chambers are often used to investigate the potential for a material to corrode or a CP&C technology to function properly. Unfortunately, these tests don't replicate true operational conditions nor do they account for the synergistic affects of other contributing factors such as atmospheric pollutants or chemical exposure during service. This is what makes conducting a corrosion analysis such a challenge.

Figure 4   Various Army Systems Exposed to the Marine Environment during Transportation

Figure 5   Munitions Stored in a High Humidity Environment

Perhaps the best source of information to address both the expected operational environment and the potential for corrosion problems is to consult the literature to determine whether there is documented field service experience on a legacy system similar to the one being designed. Natural aging information of a system or structure operated within the same or a very similar environment to that being designed can provide some excellent insight as to what to expect for the new system. Also, if materials used on the older system have shown the potential to corrode, then there are some lessons learned that can used to avoid the use of problematic materials in the new system.

One may be tempted to minimize future corrosion problems by relying solely upon legacy technology by building new systems out of the same materials that their predecessors were made from. In some situations this may be an entirely acceptable approach. However, new materials are often innovative in nature and a designer can exploit their improved properties that provide performance advantages over a legacy or competing system. For situations where no laboratory or in-service data is available designers shouldn't be deterred from the use of new materials. The known environmental conditions within an existing system of a similar nature can be used as a guide to ascertain whether future corrosion problems can be expected with the new materials that provide additional performance capabilities. This perspective can lead to the development of a test protocol to determine whether the new material possesses the necessary corrosion resistance. Additionally, effective corrosion prevention and control strategies may be able to be employed with a new material to provide the necessary corrosion protection.

1.3 Design Approaches to Ensure Corrosion Resistance

There are other considerations in the design process in addition to selecting corrosion resistant materials and associated CP&C technologies. Even with proper materials selection designers can unintentionally exacerbate the likelihood of corrosion by creating conditions that favor its occurrence. For instance, by not including drainage holes in a structure that is subjected to rain or wash water, the liquid can become trapped and accelerate the corrosion process in an entirely unanticipated location and fashion. Other considerations include using materials that won't wick moisture. It's important to avoid, if at all possible, the use of wood, paper, cardboard, open cell foams, and sponge rubbers in systems that operate in wet environments or in environments that have a high humidity. These materials have a tendency to retain water and thus provide it to an adjacent material that may be susceptible to corrosion.

Another significant design consideration involves the junction where two adjacent components come together. Known as faying surfaces, these areas can see sufficient relative movement between each other so that protective surface layers at the joint may wear away, exposing the underlying material directly to a corrosive environment. To protect faying surfaces, proper sealing materials (tapes, films, sealing compounds) and primers must be employed.

The intimate contact of two adjacent materials can be the causative factor for another corrosion mechanism. *Galvanic corrosion*, one of the eight main forms of corrosion to be covered later in this report, results when dissimilar metals come in contact with each other and are exposed to corrosive conditions. One of the best ways to prevent these materials from corroding further is to electrically insulate them through the use of coatings at the interface between them. A nonconductive coating will prohibit electrons from moving between the two materials, thus stopping the oxidation process.

Another important aspect is to design the system or structure for maintenance access. It is vitally important that inaccessible areas be minimized so that maintenance personnel can both inspect the areas for corrosion and reapply CP&C materials or replace components if necessary. For those situations where inaccessible areas are unavoidable, then it is even more important that a proper upfront analysis be conducted to ensure that proper corrosion resistance can be sustained to preclude unanticipated damage that would be extremely costly to address after the system is fielded. When analyzing maintenance access requirements, the designer should consider that nondestructive evaluation techniques will be needed to detect hidden corrosion at some point during the operational use of the system. The structure must be designed to accommodate the necessary testing apparatus to preclude hidden corrosion from creating an unsafe or unreliable system.

1.4   Design Pitfalls

As it relates to corrosion prevention and control there are several pitfalls that can and do occur from time to time. Unfortunately, designers seldom have a strong background or understanding of corrosion. To many engineers corrosion is a single process and they don't recognize that highly accelerated, localized corrosion mechanisms even exist. It is also a mistake to assume that two seemingly identical materials that may have the same composition (relative amounts of elemental constituents) but have been processed differently, for example with different heat treatments, may likely exhibit the same corrosion rates. The potential for a material to corrode is often strongly influenced by the processes used to create it.

Another pitfall is that equations used to predict corrosion rates are inappropriately used. If a designer, who lacks the necessary understanding of corrosion, considers all corrosion to be the same single process, then they are prone to making the mistake of applying an equation developed for a well-understood and predictable process such as *uniform corrosion* to predict the rate of degradation for a highly accelerated localized form of corrosion like *pitting corrosion*. Localized corrosion like *pitting* or *crevice* corrosion experience extremely high corrosion rates in very small and often hidden locations. The rates of corrosion for these mechanisms vary widely from one case to another; hence they don't lend themselves at all to predictive methodologies. Engineers not understanding the differences in corrosion mechanisms can and often do misapply equations which results in a strong potential for unexpected failures.

Although experimental data concerning corrosion abounds, it is often in inconsistent formats. Combined with the fact that corrosion rates are highly dependent upon usage environments, material composition, and processing history, a common pitfall is to utilize data inappropriately or incompletely. A designer with the right intentions can easily misuse data to substantiate a design decision that may lead to entirely wrong conclusions. Another contributing factor is that corrosion data, especially that relating to natural aging, is scattered and available from many different sources. This type of data is seldom consulted, and consequently design decisions don't fully benefit from the lesson's learned. The net result in both cases is that a system, structure or component will possess far worse corrosion characteristics than initially believed or desired.

1.5   Conclusions

For the uninitiated one might gain a view after reading this discussion that corrosion cannot be prevented without painstaking and extraordinary measures. It is important to point out that the

goal of materials selection isn't to eliminate corrosion in all circumstances, but to manage and minimize it. The challenge to effective corrosion prevention and control is to strike a balance to ensure adequate inherent corrosion resistance and ease of maintenance while at the same time balancing cost. Cost includes not only the design time required to analyze and select the most appropriate material, but also the material itself. In general, the inherently corrosion resistant materials are typically more expensive than those that are less so. During the design process the engineer must choose the material that provides the best combination of performance, including corrosion resistance, which will ensure that the article will adequately perform its function over the intended lifespan within fiscal constraints.

Reducing risk on new acquisition has to be an important concern for all stakeholders in the acquisition process. This risk can take several forms, all of which can seriously impact readiness, especially if unanticipated but completely avoidable corrosion problems occur during service. One of the biggest problems often seen is unexpected maintenance, reliability problems, and premature wearout. Having to replace components or even entire systems because they experience unexpected corrosion is clearly an unaffordable prospect that significantly impacts total ownership costs as well as the ability of our troops to effectively accomplish their military objectives. Even more important is that hidden corrosion can and will cause unexpected failures that can be catastrophic in nature. Correcting these problems before they occur can be accomplished if a detailed analysis of corrosion prevention and control becomes a featured part of the materials selection process.

This guidebook has been written to provide acquisition personnel with the fundamental background they need to understand the cause, effect, and ramifications of corrosion. It provides enough information so that a program manager or engineer in a technical oversight role may better understand the science of corrosion, causative factors including operational environments, and mitigation processes, especially the importance of materials selection for both construction materials as well as corrosion preventative compounds. A glossary in an appendix to this report provides a definition of corrosion-related terminology that may be of value to acquisition professionals involved in corrosion prevention and control activities.

This book was not written to train engineers in corrosion but rather provide enough technical background so that a manager or engineer in a program management role will have enough knowledge to oversee the materials selection process to ensure that corrosion tolerant structures, systems, and equipment, including infrastructure, are delivered to the end-user. With adequate attention to corrosion up-front during design, the probability that corrosion resistant systems and structures will result shall be much higher. Anything that ages in a predictable fashion is much easier to maintain and less costly to operate. In addition, should conditions warrant, it is also easier to extend their service lives, which in today's military environment seems to be an ever-increasing prospect.

2.0 Selecting Materials for Improved Corrosion Resistance

Seldom can a designer select the perfect material for an application since in general there will always be tradeoffs and other considerations that must be made. This is especially true when these considerations include environmental degradation such as corrosion. Other factors that complicate the analysis include performance variables such as mechanical, electrical or thermal properties; availability and maintainability; and cost. There are numerous references to traditional materials selection practices and methods that designers can consult to help them sort through traditional design requirements. However, one of the most difficult considerations is to down-select from a list of candidates a material that optimally balances performance variables along with corrosion resistance.

Many engineers consider 'materials selection' to be the process of selecting the materials needed to construct an item. This is a narrow view. During materials selection the designer should also determine the corrosion prevention and control practices and materials needed to ensure acceptable corrosion resistance over a system's life-cycle. This strategy will help to ensure that corrosion-related maintenance requirements are minimized and predictable, thus reducing overall life-cycle costs and ensuring acceptable system readiness rates. Reasonable (and budgeted) life-cycle costs and high readiness rates (due to reduced maintenance requirements) are two of the most important attributes desired by the program manager responsible for a system.

In an ideal world, materials engineers and corrosion specialists would always assist designers with material selection tasks to ensure that components and systems are designed with longevity in mind. In the real world however, this is not always the case. Designers often select the materials of construction themselves, with their decisions primarily based on meeting critical performance requirements. Other factors, such as corrosion prevention and control, are often given minimal consideration. This observation is not universally true, however, as the aerospace industry generally pays more attention to materials selection.

A material's inherent corrosion resistance is largely determined by its elemental composition, but also by its processing history, surface morphology, geometry, and in some cases its size. Consequently, two very similar materials may have quite different resistances to corrosion. Selecting the 'best' material, from a corrosion standpoint, is not a cut-and-dried process. Numerous factors need to be considered and there is no single path to making an informed selection. Ultimately, designers must rely upon their best 'engineering judgment' to select the optimum material(s), considering corrosion resistance in balance with traditional performance requirements including mechanical, thermal, physical, and electrical properties. Ultimately other factors including availability, maintainability and cost must be considered before making the final selection.

Because corrosion science is a complicated matter, it doesn't easily lend itself to the development of a simplified selection process. Many material performance criteria can be expressed numerically, in terms of a threshold, a range, or even an equation. Choosing material candidates to meet such performance requirements is usually a straightforward process. Considering the forms of corrosion as well as the selected corrosion prevention and control (CPAC) measures that might influence the in-service behavior of a material candidate is a highly qualitative process that requires circumspection.

This chapter provides designers with a 'road map' covering the major steps needed to assess the effects of corrosion during the material selection process. Following these steps should help to reduce the instances and extent to which corrosion occurs, even without being an expert in corrosion. You should note, however, that successfully following the process described here will require you to acquire information from elsewhere in this book and from other sources. Additional data is required to provide the technical basis needed to correctly address the various decision steps about to be described. The process presented here refers to down-selecting from a candidate list of materials; however, even if there is only a single material on the candidate list, the process should still be followed to ensure that an appropriate corrosion analysis is performed for that material.

The remaining chapters of this handbook mirrors and supports the steps outlined in this 'road map'. Additional information resources will also need to be consulted to obtain specific corrosion related information on the candidate materials. In critical situations where corrosion cannot be tolerated, it is always best to consult subject matter experts that have the credentials to ensure that all aspects of potential corrosion mechanisms are thoroughly investigated.

2.1 Corrosion Prevention and Control Considerations

Corrosion prevention and control doesn't end after materials selection has concluded. Rather, it continues through both the acquisition and sustainment phases of a product's lifecycle. Figure 6 represents some of the factors affecting corrosion across a system's lifetime. Corrosion prevention and control should be considered during the design concept generation phase and continue through the materials selection process. Preventive maintenance and monitoring/inspection plans should be developed during the detailed design phase and maintained and updated as needed during sustainment.

Figure 6 highlights the significant considerations that must be made when designing corrosion resistant components and/or systems. The following sections provide additional detail concerning these considerations.

Design Considerations: The particular design geometry is important as areas where water and/or debris may accumulate can experience increased corrosion rates. Simply drilling holes in structures to allow drainage of water can help to mitigate this problem. Eliminating sharp corners will help reduce crevice attack. Also, providing accessibility, when possible, to corrosion prone areas for cleaning and maintenance is important. The geometry of components will also influence erosion corrosion for systems exposed to flowing corrosive fluids. This includes directional changes in piping and the access ports for chemicals that are added into systems. The interfaces between adjacent materials or components may contribute to corrosion in the form of galvanic, crevice, and intergranular corrosion. The relative sizes of two materials affects the current density between them which factors into galvanic corrosion rates. Fastened joints are areas which can trap electrolytes resulting in crevice attack. Welded and brazed joints can increase susceptibilities to intergranular corrosion in certain alloys/heat treatments. The design along with the operation of the system will determine the applied stress to components that may result in stress corrosion cracking (SCC) or corrosion fatigue. And finally, systems operated in close proximity to electrically conducting structures may experience stray-current corrosion. Further elaboration on the corrosion mechanisms and mitigating factors discussed above are found elsewhere in this book.

Corrosion Prevention And Control Considerations

Design	Material Selection	Processing/Manufacturing	

• Geometry
• Material Interfaces
• Relative Sizes
• Joints
  o Fastened
  o Welded
  o Brazed
• Applied Stresses
• Stray currents
	• Base Material
	  o Metals
	
	  o Organics
	  o Ceramics
	  o Composites
	• Heat Treatments
	• Corrosion Prevention & Control
		• Surface treatments
		  o Conversion Coatings
		  o Cleaning
		  o Anodization
		  o Shot/Shock Peening
		• Cold Working
		  o Fasteners
		• Polishing
			• Coatings
			  o Claddings
			
			• Quality Control
			  o Impurities
			  o Defects
			  o Surface Condition
			  o Joints

Preventative Maintenance	Monitoring / Inspection

• Storage conditions
  o Humidity
• Cleaning
  o Agents
  o Abrasives
  o Inhibitors
  o Biocides
• Coating removal
• Recoating
• Corrosion Preventative
	• Electrochemical sensors
	  o Visual inspection
	• Weight loss coupons
	• Bacteria counts/cultures
	• NDI
	  o Thickness
	  o Cracks

Figure 6   Corrosion Prevention and Control Considerations

Material Selection Considerations: The cost of maintaining a system is significantly influenced by the initial choice of materials, heat treatment methods, and corrosion prevention and control measures/materials. The choice of heat treatment is crucial as numerous corrosion forms including stress corrosion cracking, corrosion fatigue, intergranular, and exfoliation corrosion can be strongly influenced by a material's processing history. Selection of base materials for corrosion resistance is discussed at length elsewhere in this book.

Processing/Manufacturing Considerations: Processing and manufacturing methods can also affect corrosion rates through the surface roughness, quality of the material/component, and the implementation of corrosion prevention and control measures. Chemical surface treatments (conversion coatings and anodization) as well as corrosion resistant primers and topcoats will influence all forms of corrosion by providing barriers or sacrificial corroding layers to protect the base materials. Mechanical surface treatments (shot peening or laser shock peening) increase resistance to stress corrosion cracking, corrosion fatigue, and hydrogen assisted cracking (HAC). Cold working, including oversized fasteners, is another form of mechanical processing which increases resistance to cracking mechanisms. Polishing surfaces can reduce susceptibility to pitting attack and increase resistance to crack initiation. The quality of the material/component plays a role in that any impurities within a material and any defects on its surface or in a joint may increase the risk of corrosion.

Preventive Maintenance Considerations: Employing a preventive maintenance schedule where a vehicle or structure is periodically inspected and cleaned, as necessary, will help reduce

corrosion. Salt and debris buildup on vehicles or structures, for example, can accelerate corrosion. Therefore, routinely washing them to remove the contaminants is a sound practice. In addition, regularly touching up protective coatings or reapplying corrosion preventive compounds (CPCs) will help reduce instances of corrosion. Surface preparation is critical to coating adhesion, although in most cases, recoated systems will never adhere as well as the original coating deposited in a controlled environment.

Often overlooked during a corrosion analysis is the period in which a system is not in operation. Some materials, such as stainless steels, are resistant to high velocity flowing liquids and thus are used for certain piping applications. However, these same materials can be susceptible to pitting, crevice, and microbiologically influenced corrosion (MIC) under stagnant conditions. Introducing inhibitors and/or biocides into piping during downtimes can reduce these forms of corrosion. Storage conditions are also very important. Reducing the relative humidity below 60% can significantly reduce corrosion of systems during storage. Reducing the temperature in hot/humid climates will also be beneficial.

Monitoring/Inspection Considerations: Monitoring and inspection are often essential preventive maintenance procedures. Visual inspection has been widely practiced throughout most any system. Hidden corrosion requires a number of different tactics dependent upon the system. Borescopes and fiberscopes are used to visually inspect the inside of some systems through access ports. Electrochemical sensors are used to monitor the corrosivity of the operating environment. Bacteria counts and cultures are used to monitor microbiological activity and to regulate the use of biocides. Corrosion coupons are a low technology technique of placing metal samples within the system and periodically measuring their weight loss. Personnel responsible for maintaining critical systems may additionally use a host of nondestructive inspection methods to measure thicknesses or detect cracks.

System design, materials selection and manufacturing process actions are interrelated where each weighs in on the others as depicted in Figure 7. Historically there have been many instances where costly designs have been developed with little or no upfront consideration of materials or manufacturing concerns. This linear approach to developing a new component or system can lead to compromises that can be avoided with a concurrent process where all issues are considered early and simultaneously.
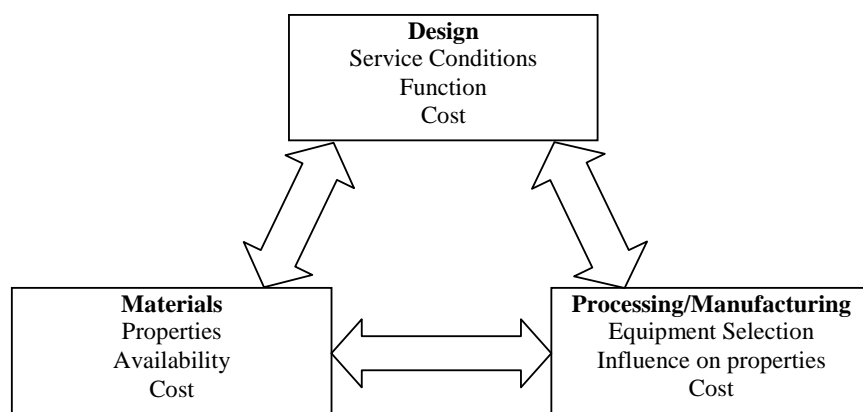
Figure 7   Interrelationship between Design, Materials Selection, and Processing/Manufacturing

2.2 Incorporating a Corrosion Analysis into a Traditional Materials Selection Process

There are a handful of material selection strategies that are used by designers. These strategies range from a broad selection process used to establish a list of material classes that will be applicable for a design down to detailed decision matrices to select specific materials/heat treatments. The intent of this book is not to address the various methods of selecting materials themselves. Rather, the purpose is to supplement existing processes with a 'roadmap' or process that a designer can employ during materials selection to help reduce the risk of corrosion-related problems later in a product's lifecycle. A comprehensive analysis starts by employing a traditional process to examine the mechanical, thermal, electrical, or physical requirements to determine which material class to employ and to subsequently select an initial slate of candidate materials. The process described here will be used to further examine these candidates to identify the one that possesses the best combination of performance and life-cycle costs.

Figure 8   is a generic process for conducting a corrosion analysis that supports traditional materials selection process. The body of the following sections of this chapter parallels the steps shown in this flowchart, primarily covering the "corrosion analysis" portion. Prior to the corrosion analysis, designers must first employ a traditional material selection strategy to identify a slate of candidate materials possessing the necessary physical, mechanical, thermal, and/or electrical properties to meet performance requirements. The challenge comes in ensuring that these candidates are scrutinized for their corrosion resistance before selecting the best overall candidate (Figure 9). Depending upon the criticality of the application and the design process being employed, the number of materials chosen as initial candidates will vary. For highly important decisions with strict deadlines, analyzing multiple materials simultaneously might be the most efficient approach. With this approach the project schedule would be minimally impacted should the primary candidate later be rejected for unforeseen reasons. For less critical applications it may be more practical to perform a comprehensive corrosion analysis on just a single material instead. Should this initial candidate be rejected, it would be replaced by another and the analysis would continue.

2.2.1   Step 1: Screen Materials Based on Past Experience

As shown in Figure 8, the first step in the process is to employ past experience or lessons learned to screen the initial slate of candidate materials and reject those that may have a history of severe corrosion related problems. Specifically, the analyst must determine whether there have been corrosion problems in similar applications to that being designed, and to ascertain what caused those problems to occur. The most cost-effective thing to do, from a life-cycle cost standpoint, is to eliminate from consideration any material that has caused corrosion problems in a similar application in the past, especially those problems that couldn't be controlled using affordable CPAC materials and associated maintenance procedures. One method to determine whether 'legacy' materials have corroded in a similar application is to analyze the literature or lessons-learned databases, if available, to ascertain whether a particular combination of material and application has been problematic in the past. Another way is to consult subject matter experts that have extensive experience with the design, production, and sustainment of similar legacy applications.
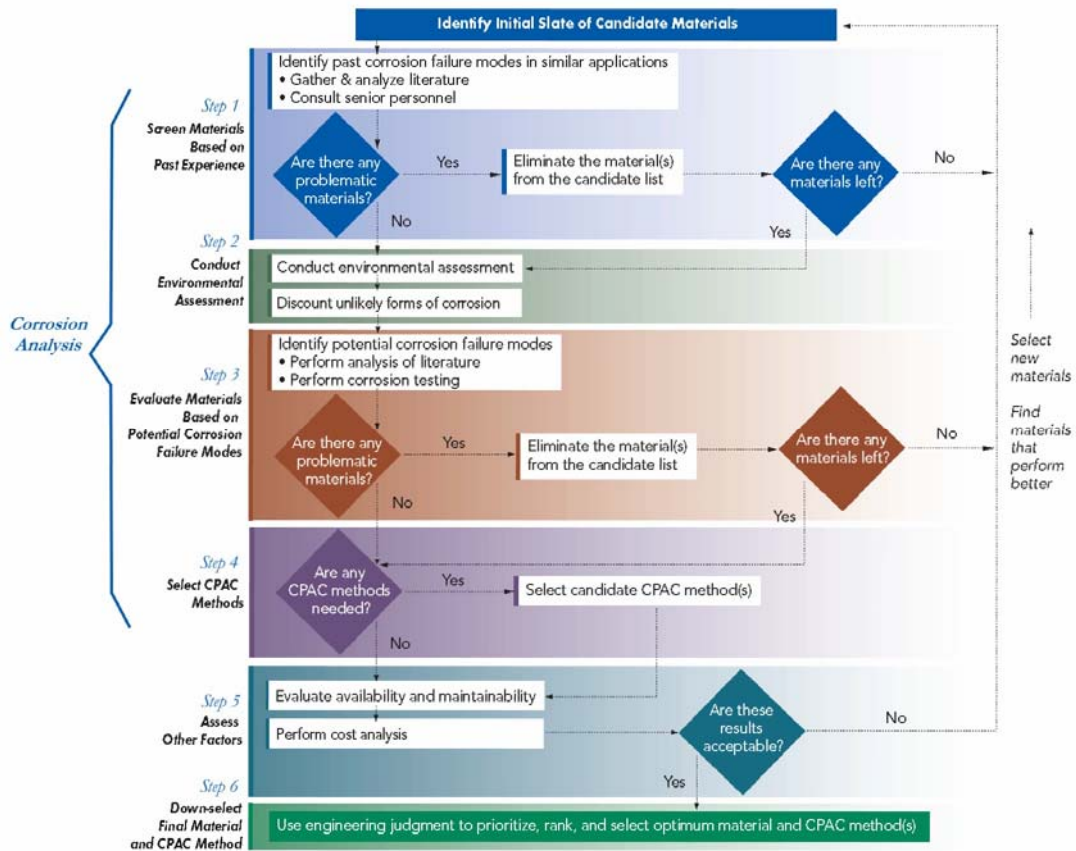
Figure 8   Generic Process for Selecting Materials for Improved Corrosion Resistance
A Roadmap to Life Cycle Cost Reduction
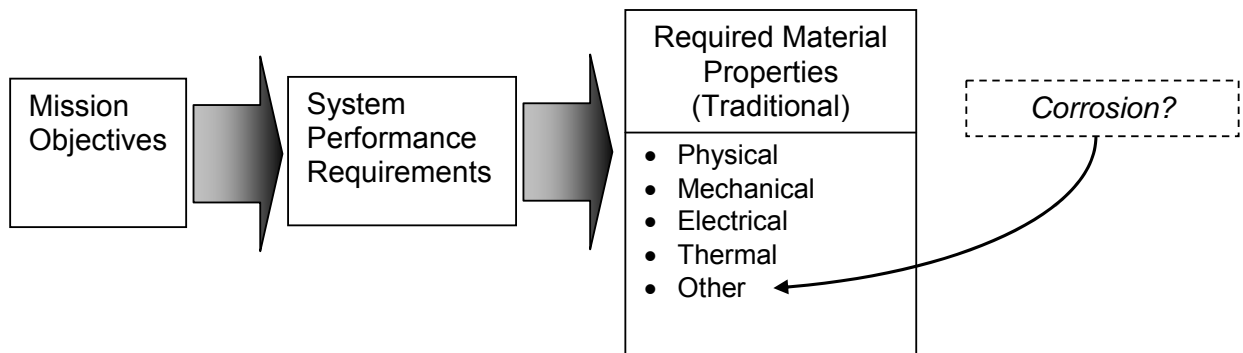
System requirements define what performance levels are needed from constituent materials. If life-cycle issues are to be addressed as part of a system's overall set of requirements, then corrosion and other time-dependent material properties must be considered.

Figure 9   Material Property Needs are Derived from System Performance Requirements

Searching for past experience or lessons-learned information on the application in question or a similar application is essential for designing in corrosion resistance. Uncovering information concerning past experience with a given application can help to identify materials that performed badly, in terms of corrosion performance. These lessons-learned can also be useful in identifying materials that had excellent corrosion performance in a given application. This information can therefore be used as a shortcut during the materials selection process for eliminating bad choices from your list of candidate materials, for identifying other materials to add to the list, or for identifying CPAC materials and practices that work best for your application.

Performing a search of past experience or lessons-learned information can also be a valuable tool for educating oneself on the many intricacies of the application's operating environment. For example, while a designer conducting materials selection might routinely consider certain environmental factors such as salinity, temperature, and humidity, they might overlook documented susceptibilities of a given application such as the effect of accumulated mud, dirt, and debris within panels, channels, or other drainage passages. The accumulation of debris can lead to the concentration of electrolytes and other corrosive agents at the surface of the metal and may lead to poultice corrosion, a type of crevice corrosion. Therefore, a search for lessons-learned information may lead to the identification of facets of the operating environment that are not immediately clear for a given application, which may in fact lead to major implications down the road in terms of choices for candidate materials and CPAC practices. 'Lessons learned', in the context referred to here, includes technical information addressed in research papers, technical reports, as well as from formal lessons learned databases.

Many lessons-learned investigations start with a search of the Internet or other data sources for the application of interest or similar applications. Searches can further be qualified by using the term corrosion within the search string to hopefully uncover any corrosion-related issues pertinent to the application. For example, if one were designing aircraft landing gear, they might quickly uncover past experience or lessons-learned information by performing a literature search using the keywords aircraft, landing gear, and corrosion. Corrosion-related searches of the literature are also useful in garnering information on the application, materials choices, historical CPAC practices, and their efficacy. However, performing a thorough search of the literature on a given application can be a time and labor intensive process. Many government and commercial organizations have taken the time to compile massive databases that include information on corrosion. A listing of several of these databases and their URLs can be seen below in Table 1. The databases listed in this table contain an incredible wealth of historical knowledge that if effectively used can reduce the risk of future corrosion related problems on products being developed.

Table 1   Listing of Corrosion Information Sources

	Information Sources	Source Description	Internet Address
US Government Data Sources	DoD Advanced Materials, Manufacturing and Testing Information Analysis Center (AMMTIAC)	Technical Library and NAMIS Database	http://ammtiac.alionscience.com/InfoResources/docsearch.html http://namis.alionscience.com/
	Defense Technical Information Center (DTIC)	Public and Private STINET Database	http://stinet.dtic.mil/info/s-stinet.html (public STINET) http://www.dtic.mil/dtic/registration/index.html (Private STINET-limited distribution documents)
	Department of Energy (DOE)	Energy Citations Database	http://www.osti.gov/energycitations/index.jsp
	National Aeronautics and Space Administration (NASA)	Aeronautic and Space Database	https://www2.sti.nasa.gov/login/wt/
	Federal Aviation Administration (FAA)	Library Search Engine	http://www.faa.gov/library/
	National Institute of Standards and Technology (NIST)	NIST Webspace Keyword Search Engine	http://www.nist.gov/search.htm
	National Aeronautics and Space Administration (NASA)	Lessons Learned Information System (LLIS)	http://search1.nasa.gov/nasasearch/llis/search/search.jsp
	Department of Energy (DOE)	Lessons Learned Database	http://www.eh.doe.gov/DOEll/index.asp
	Center for Army Lessons Learned (CALL)	Lessons Learned Database	http://call.army.mil/
	Department of Energy (DOE)	Lawrence Livermore National Laboratory (LLNL) Lessons Learned Database	http://www.llnl.gov/es_and_h/lessons/lessons.shtml
	Naval Postgraduate School	Links to Lessons Learned Databases throughout the DoD and Federal Government	http://library.nps.navy.mil/home/lessons.htm
	Marine Corps Center for Lessons Learned	Lessons Learned Database	http://www.mccll.usmc.mil/
	Navy Lessons Learned System (NLLS)	Lessons Learned Database	http://www.nwdc.navy.mil/NLL/NLL.aspx

Table 1, continued - Listing of Corrosion Information Sources

	Information Sources	Source Description	Internet Address
Professional Societies and Other Sources	NACE International (The Corrosion Society)	NACE Store Product Search Engine	http://www.nace.org/nacestore/search.asp
	ASM International (The Materials Information Society)	ASM Website Search Engine	http://www.asm-intl.org/
	SSPC (The Society for Protective Coatings)	SSPC Online Store Search Engines	http://www.sspc.org/books/bookstore.html
	SAE International (Society of Automotive Engineers)	SAE Website Search Engine	http://www.sae.org/jsp/jsps/advancesearch.jsp\
	SME (The Society of Manufacturing Engineers)	SME Website Search engine	http://www.sme.org
	ASTM International (source for standards)	ASTM Standards Search Engine	http://www.astm.org
	ASCE (American Society of Civil engineers)	ASCE Online Research Library	http://www.ascelibrary.org/
	ECS (Electrochemical Society)	ECS Website Search Engine	http://www.electrochem.org/search.htm
	Swedish Corrosion Institute	Webpage with Report Listing	http://www.corr-institute.se/english/reports/Rep_list_e.html

The DoD and other U.S. Government agencies have invested considerable funds into researching corrosion modes, and mitigating their effects in existing applications. Much of this work has been recorded in technical reports that are available from AMMTIAC and from our sponsor, the Defense Technical Information Center (DTIC). NASA and DOE also have extensive corrosion resources. The reports available from these organizations are excellent sources of relevant data to consult when performing material selection. In many cases they contain "lessons-learned" information that discusses corrosion in very similar applications and operational environments to those you may be considering. Other sources of information include reference books, handbooks, and other products available from professional societies. These sources typically have very good data related to coupon level testing, as well as discussions on problematic materials. Unlike technical reports that address very specific issues that may be relevant to your program needs, these resources typically offer more general information. Table 3 and Table 4 provide an indication of the extensive amount of technical reports and the subject they cover that are available through DoD and other government databases.

Table 2   Information Resources

Information Source		Type of Information	Number of Corrosion Related Reports and Papers	Available Search Engine?	Downloadable PDFs?	Free Service or Fee Based?	Access Restrictions?
US Government Data Sources	AMMTIAC*	Papers, Reports, Databases	22,972	Yes	Yes (Limited)*	Fee for subscription to controlled-access databases and for ordering hardcopies	Yes, Access to Limited Distribution portion of holdings is controlled
	DTIC	Papers, Reports	37,781	Yes	Yes	Fee for ordering hardcopies	Yes, Access to Limited Distribution portion of holdings is controlled
	DOE	Papers, Reports	42,745	Yes	Yes	No	No
	NASA	Papers, Reports	27,589	Yes	Yes	Fee for ordering hardcopies	Yes, Access to database is limited to NASA employees, Government employees, and NASA contractors
	FAA	Papers, Reports	>500	Yes	Yes	No	No
	NIST	Papers, Reports	>1000	Yes	Yes	No	No
Professional Societies and Other Sources	NACE	Books, Papers, Reports, Standards, Databases, Videos	74,000	Yes	Yes	Fee for downloading/ordering products/reports/databases/standards	No
	ASM	Books, Papers, Reports, Standards, Videos	140	Yes	Yes	Fee for downloading/ordering products/reports/databases/standards	No
	SSPC	Books, Papers, Reports, Standards	>100	Yes	Yes	Fee for downloading/ordering products/standards/guides/reports/specifications	No

Table 2, continued - Information Resources

Information Source		Type of Information	Number of Corrosion Related Reports and Papers	Available Search Engine?	Downloadable PDFs?	Free Service or Fee Based?	Access Restrictions?
Professional Societies and Other Sources	SME	Papers, Reports	253	Yes	Yes	Fee for downloading/ordering products/standards/guides/reports/specifications	No
	SAE	Papers, Reports, Standards	2671	Yes	Yes	Fee for downloading/ordering products/reports/databases/standards	No
	ASTM	Standards	>700	Yes	Yes	Fee for downloading/ordering products/standards/guides/reports/specifications	No
	ASCE	Papers, Reports	>350	Yes	Yes	Fee for downloading/ordering products/guides/reports	No
	ECS	Papers, Reports	>1000	Yes	Yes	Fee for downloading/ordering products/guides/reports	No
	Swedish Corrosion Institute	Books, Papers, Reports	>150	No	Yes	Fee for downloading/ordering products/guides/reports	No

* - AMMTIAC currently has a scanning and database development project underway that will result in over 14,679 corrosion-related electronic documents being available for download from the AMMTIAC/NAMIS websites.

Table 3   Document Hits by Keyword (within Corrosion) for Various Government Databases (as of 2003)

		AMMTIAC	DROLS	NASA	DOE	DOT	DOC*	TOTALS**
	Total Available Corrosion Reports:	22972	37781	27589	42745	4256	6697	142040
By Application:								
	Aircraft	1645	4272	2104	442	68	444	8975
	Space	792	1650	508	1146	122	198	4416
	Ship	1045	1907	63	530	519	104	4168
	Submarine	101	498	11	49	14	9	682
	Vehicle	336	1295	107	528	361	99	2726
	Infrastructure (bridges, dams, pier, pipeline)	368	779	456	970	1853	412	4838
	Industrial	632	9633	508	2958	108	284	14123
	Electronics	408	1791	349	882	46	54	3530
By Mechanism:								
	Uniform OR General	582	332	959	827	451	578	3729
	Galvanic	901	1157	382	350	168	129	3087
	Crevice	1101	1171	315	564	105	147	3403
	Pitting	2573	2828	1085	1487	212	382	8567
	Intergranular	1800	2015	1524	1574	32	226	7171
	Selective Leaching OR Dealloying	26	44	21	43	5	6	145
	Stress Corrosion Cracking	2546	3607	3981	1910	228	638	12910
	Erosion	770	1340	907	13630	181	260	17088
	Corrosion Fatigue	1147	1484	855	536	213	549	4784
	Hydrogen	2351	3187	1768	7660	133	474	15573
	Microbiological (biofouling)	111	171	44	75	14	50	465
	Exfoliation	304	343	146	46	4	14	857
	Fretting	190	226	444	117	20	40	1037
	High Temperature Corrosion	170	412	381	177	19	1011	2170
	Oxidation	2224	6000	2419	5814	170	594	17221

Table 3, continued   Document Hits by Keyword (within Corrosion) for Various Government Databases (as of 2003)

	AMMTIAC	DROLS	NASA	DOE	DOT	DOC*	TOTALS**
Total Available Corrosion Reports:	22972	37781	27589	42745	4256	6697	142040
By Environment:							
Environmental	6700	9362	1285	3056	1182	835	22420
Atmospheric OR atmosphere	1368	1836	969	1988	248	325	6734
Marine	1180	6046	482	563	595	214	9080
Seawater	1962	2802	5342	735	426	145	11412
Tropical	64	252	45	27	16	2	406
Space	786	1652	508	1146	122	198	4412
High-Temperature	2104	3596	3716	7916	100	1012	18444
Industrial	629	9633	508	2958	108	284	14120
Chemical	4708	5425	2842	19844	713	1309	34841
By Protection Method:							
Coating	4195	3806	1716	5654	878	591	16840
Sealant	158	309	35	42	33	16	593
Primer	346	699	162	67	137	66	1477
Inhibitor	939	1548	313	853	334	116	4103
Cathodic	1389	1929	658	1275	613	299	6163
Anodic	1997	2412	856	953	136	139	6493
Protect*	2891	6435	3624	8500	2380	1297	25127
Prevent*	1034	2031	3609	1739	1193	688	10294
Passivation	968	1037	389	823	48	107	3372
Mitigation	29	136	38	221	64	67	555
Control	2219	3831	1492	5303	864	903	14612

Table 3, continued   Document Hits by Keyword (within Corrosion) for Various Government Databases (as of 2003)

	AMMTIAC	DROLS	NASA	DOE	DOT	DOC*	TOTALS**
Total Available Corrosion Reports:	22972	37781	27589	42745	4256	6697	142040
By Testing and Inspection							
Testing	3349	19099	1853	11560	2088	1399	39348
Accelerated	147	324	0	31	190	92	784
Natural (Field Test, In-service Test)	218	378	140	121	239	145	1241
Inspection	628	2655	634	1439	463	516	6335
Monitoring	301	1165	362	2013	375	359	4575
Non-destructive	550	2107	618	1274	151	310	5010
Neutron Radiography	22	86	30	42	3	12	195
Digital Radiography	2	8	3	5	0	1	19
Guided Wave Ultrasonic	0	4	0	9	0	3	16
Microwave AND NDE	9	9	1	3	2	18	42
Magneto-optic Eddy Current Imaging	1	8	7	1	0	0	17
AC Magnetic Bridge Scanning	0	1	0	0	0	0	1
Multi-frequency Eddy Current	0	0	0	2	0	1	3
Thermal Imaging	9	30	10	41	3	24	117
Optically Aided Visual Inspection	1	2	1	0	0	0	4
By Material Class							
Metal	7138	15331	5694	31255	874	1218	61510
Ceramic	1148	2195	850	11120	63	380	15756
Polymer OR Plastic	1027	4099	44715	2436	493	310	53080
Composite	1750	5974	1040	1496	417	470	11147
Electronic	350	1782	293	904	30	109	3468
Optical	530	1075	599	877	28	172	3281
By Specific Metals							
Steel	9417	13163	3466	14596	2573	1615	44830
Aluminum	6084	8844	4808	3959	369	748	24812
Titanium	3477	4399	2184	3981	108	383	14532
Nickel	4516	6007	2577	9329	196	514	23139
Superalloy	695	803	523	396	8	19	2444

Table 3, continued   Document Hits by Keyword (within Corrosion) for Various Government Databases (as of 2003)

	AMMTIAC	DROLS	NASA	DOE	DOT	DOC*	TOTALS**
Total Available Corrosion Reports:	22972	37781	27589	42745	4256	6697	142040
By Specific Metals							
Magnesium	1585	2227	780	1467	140	119	6318
Copper	1597	2675	131	2954	230	446	8033
Zinc	875	1660	720	1128	325	200	4908
Tin	223	559	249	1233	19	76	2359
Cadmium	262	520	162	417	16	46	1423
Refractory Metal	136	326	322	454	0	31	1269
By System Component							
Joint	1119	2003	273	916	310	139	4760
Lap	175	191	63	4	2	19	454
Butt	77	93	10	7	14	3	204
Weld	2460	3313	394	972	399	140	7678
Gasket	47	108	17	36	6	7	221
Seal	95	1305	114	297	185	55	2051
Fastener (bolt, rivet)	210	1205	228	68	136	51	1898
Stiffener	20	36	8	0	5	4	73
Valve	153	463	75	323	76	42	1132
Connector	91	347	17	23	26	9	513
Skin	256	410	189	53	20	46	974
Hull	168	636	17	48	281	31	1181
Armor	85	215	25	26	6	16	373
Bearing	470	670	287	208	82	187	1904
Housing	87	317	30	85	25	19	563
Engine	4302	2966	790	517	237	134	8946
Piping	408	844	118	1164	94	187	2815

* Since 1990
** Most likely inflated as documents may be found in multiple libraries.

Much of the information needed to identify and eliminate problematic materials from consideration can be found in the technical literature. Literature investigations are also useful for identifying design details to be avoided and for helping select the appropriate CPAC practices needed to protect the chosen material and ensure that it performs as desired. It's important to perform these investigations upfront during the design process to preclude unacceptable life-cycle costs or catastrophic failure from occurring.

In some situations it might be the case that corrosion susceptibility data concerning a specific material being considered doesn't exist. In these situations it may be necessary to perform corrosion testing to ascertain the candidate material's behavior in the intended environment. However, the cost as well as the time required for conducting tests must be carefully considered since they could affect the development schedule. There have been many past instances where designers simply assumed that the needed data didn't exist so they either neglected the analysis completely or they jumped directly into corrosion testing. This can often be a wasteful strategy since the literature is rich with corrosion data.

2.2.2   Step 2: Conduct Environmental Assessment

As shown in Figure 8, the second step employed when performing a corrosion analysis is to assess the environment to which the material will be exposed. After a candidate material (or materials) has been selected and the obvious problematic materials have been rejected, based upon a review of past experience or lessons-learned (step 1), the next step is to analyze the environment in which the application will operate. When considering the operational environment, many may automatically consider exposure to atmospheric, industrial, or marine conditions as the corrosion inducing factors. The designer must also consider the corrosive microenvironments that may occur during operation. For instance, the build-up of scale within storage tanks and piping may result in situations where corrosive ions can accumulate and precipitate hidden corrosion. The same can be said for structural details used in the construction of a system including lap joints, gaskets, and enclosed places that cannot be accessed. These design details and operational conditions are known to concentrate ions, thus making a corrosive microenvironment specific to certain regions within an application.

Designers should thoroughly analyze the operating conditions the entire system will be subjected to and determine the potential combinations of design details, temperature, humidity, and chemical exposure that may be present during operation. The designer should also consider the conditions the system may experience throughout its life-cycle including maintenance, storage, and transportation. For example, ground vehicles being transported by ship over the ocean can become sprayed with saltwater and subsequently experience corrosive attack that can rapidly destroy them. When conducting the corrosion analysis, designers should consider both the micro- and macroenvironments to determine the specific conditions that candidate materials will be exposed to during their service.

A comprehensive analysis of the operating environment can be an extensive undertaking. Therefore, depending upon the time and resources available, the extent of the analysis could range from general to detailed using a tiered approach. It is most important to first define the general operating conditions (e.g. atmospheric, immersed in liquid, buried, etc.). From there more detail can be added on: industrial atmospheric, tropical seawater, etc. A detailed environmental assessment could include specifics on pH, pollutants, temperature, and other

relevant factors, as illustrated in Figure 10. Design details should not be overlooked since they certainly can initiate the microenvironments responsible for triggering specific corrosion modes.

Environmental Assessment

Identify main constituents with concentrations

Identify impurity constituents with concentrations

Identify temperature, humidity, pressure, and pH

Identify the degree of aeration

Identify the velocity and/or agitation properties

Identify the applied stresses

- Fuels
- Lubricants
- Cleaning agents
- Biocides
- Inhibitors

- Atmospheric
  - Rural
  - Industrial
  - Marine
- Water
  - Freshwater
  - Saltwater
- Soil
  - Type
  - Resistivity

Figure 10   Environmental Assessment Process

Once a firm understanding of the operating environment is garnered, several forms of corrosion lend themselves to easy elimination via answering simple environmental-based questions. These forms of corrosion include: erosion corrosion, high temperature corrosion, molten salt corrosion, liquid/solid metal embrittlement, stress corrosion cracking, and corrosion fatigue. By answering simple questions about the operating environment, these forms of corrosion can often be discounted as unlikely to occur. A listing of these corrosion forms and the associated elimination question can be seen in Table 4.

As an example, erosion corrosion occurs when a corrosion prone material is exposed to a flowing corrosive fluid. If the application being designed will not be exposed to a flowing fluid, then erosion corrosion is irrelevant and can be discounted. However, one must give careful thought when answering these deceptively simple questions, such as that for erosion corrosion. For example, at first glance if one is selecting materials for a power generator application on dry land they might be tempted to say that their application is not subject to a flowing corrosive fluid. Based on this assumption, the person might not consider erosion corrosion as being likely to occur. However, if the power generator is water-cooled then any material within the system that comes into contact with the coolant may be subject to a flowing corrosive fluid. This is because as coolants mix with contaminants found within the system they can become corrosive over time.

Erosion corrosion is common in piping, cooling systems, valves, boiler systems, propellers, impellers, as well as numerous other components. An example of erosion (cavitation) corrosion of a brass pump impeller can be seen in Figure 11. Here the soft copper oxide protective layer was eroded enabling corrosion of the base metal.

Table 4   Eliminate Irrelevant Corrosion Failure Modes

Form of Corrosion	Elimination Question *If the answer is*: No) The form of corrosion unlikely to occur Yes) It should be explored as likely form of corrosion
Erosion Corrosion	Is the system, component, or material exposed to a flowing corrosive fluid?
High Temperature Corrosion	Is the system, component, or material subjected to a high temperature gaseous environment?
Molten Salt Corrosion	Is the system, component, or material subject to molten or fused salts?
Liquid/Solid Metal Embrittlement	Is the system, component, or material subject to a liquid metal? (e.g. Mercury)
Stress Corrosion Cracking	Is the system, component, or material subject to a constant stress?
Corrosion Fatigue	Is the system, component, or material subject to a cyclic stress?

Figure 11   Erosion Corrosion of a Brass Pump Impeller

2.2.3   Step 3: Evaluate Materials Based on Potential Corrosion Failure Modes

The third step in the process is to evaluate materials based on potential corrosion failure modes. The identification of the relevant forms of corrosion is one of the most important steps in the process. It is also not an easy one since there is often a lack of concise understanding of all the different corrosion forms that should be considered. Therefore, lessons learned information can be a valuable method of identifying as well as rating the importance of the forms of corrosion to the application/environment. However, lessons learned information should not be entirely relied upon, because a change in materials or operational factors can lead to alternate forms of corrosion

not previously encountered. Hence, an analysis should consider all potential forms of corrosion for the application/environment, while making use of available lessons learned information.

Most applications/environments will be susceptible to one or more of the major or minor forms of corrosion (Table 5). Table 5 provides a listing of the corrosion forms covered in this handbook.

Table 5   Forms of Corrosion

Form of Corrosion		Definition	When to consider
Major Forms	Uniform (general)	A form of corrosion that occurs uniformly over the entire exposed surface of a metal.	Susceptible alloys
	Pitting	A form of localized corrosion that occurs when a corrosive medium attacks a metal at specific points and results in deep cavities in the metal.	Susceptible alloys
	Crevice	A form of corrosion that occurs when an electrolyte becomes trapped and stagnant in particular locations such as in joints, corners, and under debris.	Joints, corners, and where debris may accumulate
	Galvanic	A form of corrosion resulting from the formation of a galvanic cell by the galvanic coupling of dissimilar metals (metals having different electrical potentials), which are exposed to an electrolyte.	Two dissimilar metals in direct contact or separated but in electrical contact
	Erosion Corrosion	The increased rate of deterioration and loss of a material due to the combined effects of corrosion and the repeated motion of the surrounding environment.	Moving corrosive or erosive liquid
	Intergranular	A form of corrosion that attacks grain boundaries in materials. It may occur as a result of a galvanic couple between differing phases within a material.	Susceptible alloy/heat treatments
	Selective Leaching/ Dealloying	A localized form of corrosion where a particular element within a material is preferentially attacked and extracted from the material.	Susceptible alloy/heat treatments
	Stress Corrosion Cracking	A cracking process involving the combined factors of corrosive environment and a sustained tensile stress.	Static stresses
Minor forms	Fretting	A form of corrosion caused by repetitive friction between two surfaces in sliding motion with respect to each other while exposed to a corrosive environment.	Small relative movement between two metals typically caused by vibration or repeated thermal expansion/contraction cycles
	Corrosion fatigue	The failure of a material due to the combined effects of corrosion and fatigue (cyclic stressing).	Cyclic stresses
	Hydrogen damage	Any deterioration of a material as a result of the presence of hydrogen, whether in the surrounding environment or internal to the material.	Hydrogen generation during processing or in service directly or indirectly.

Table 5, continued - Forms of Corrosion

Form of Corrosion		Definition	When to consider
Minor forms	High temperature corrosion	A form of corrosion that refers to corrosion where the electrolyte is a gas rather than a liquid.	High temperature environment
	Exfoliation	A form of corrosion that occurs in bands on the interior of the metal that is parallel to the metal's surface. This consequently forms corrosion products that cause a separation of the metal into layers. It is often considered a form of intergranular corrosion that attacks metals that have been mechanically treated to form elongated grain structures in one direction.	Rolled and extruded alloys susceptible to intergranular corrosion
	Microbiologically influenced corrosion	The occurrence or increased rate of corrosion due to metabolic activity of microorganisms present on a metallic surface.	Specific metals/environments/ applications
	Liquid metal embrittlement	The brittle failure of an otherwise ductile material when in contact with a liquid metal and subjected to tensile stress.	Extremely high temperatures (melting points)
	Solid metal embrittlement	The embrittlement of a metal when in contact with another metal that is slightly below its melting point.	Extremely high temperatures (near melting points)
	Molten salt corrosion	The occurrence of corrosion in the presence of molten or fused salts; see hot corrosion.	High temperatures/salt compounds
	Filiform corrosion	A form of corrosion that exists under organic and metallic coatings on metals, blistering the coating, and is characterized by hairline resemblance.	Thin permeable organic coatings on metals
	Stray-current corrosion	Corrosion that is caused by the unintended flow of current through a metal, where the current has originated from an external source.	Environments near electrically conducting structures
	Grooving corrosion	A specialized form of corrosion that attacks welded carbon steel piping subsequently exposed to a corrosive environment. The welding process causes a redistribution of sulfides along the weld line, resulting in a preferred attack in the weld area producing grooves in the material	Welded carbon steel piping in an aqueous environment

There are a number of actions that may be performed during material selection based upon the number of candidate materials and information gathered.   Any materials having high susceptibilities to an identified corrosion failure mode in the intended operating environment should be eliminated from the candidate pool. If no candidate materials remain, then a potential design modification may be needed or additional candidate(s) considered.

Forms of corrosion that can lead to catastrophic failure should be evaluated first so that some candidates may be eliminated before going through the entire evaluation process. The critical forms of corrosion include those associated with cracking; namely stress corrosion cracking, corrosion fatigue, and hydrogen assisted cracking. After discarding from consideration any material candidate that is likely to be prone to cracking related failure, information/data will then have to be collected on all remaining candidates including their susceptibility to the relevant forms of corrosion that may be expected. Table 6 provides a snapshot of some of the factors that will make materials susceptible or resistant to specific corrosion mechanisms. Please note that

this list is far from comprehensive so literature investigations will ultimately be required to determine which modes may be expected.

Table 6   Corrosion Rules of Thumb

Form of Corrosion	Influencing Factors	Material Characteristic	Potential for Corrosion
Uniform Corrosion	pH Temperature Ionic Contaminants Aeration Uniformity/adherence of scale Surface Finish	The material is a noble metal	The uniform corrosion mechanism does not apply to this class of materials
		The material forms a protective passive layer	Will experience uniform corrosion if the passive layer is exposed to highly oxidative conditions such as exposure to acidic chemical environments
		The material is neither noble nor does it form a passive layer	Susceptible to uniform corrosion under most environments
Galvanic Corrosion	-Dissimilar corrosion potentials between adjacent materials -Ratio of exposed anodic and Cathodic materials -pH -Aeration -Temperature	The two dissimilar metals are directly in contact	The anodic component will experience galvanic corrosion near the interface. If the anode is much smaller than the cathode the reaction will proceed rapidly
		An insulative gasket is placed between the cathode and anode	Galvanic corrosion will not occur under these conditions
		Materials used to fabricate adjacent components have similar electrical potentials	Neither material becomes cathodic or anodic. Galvanic corrosion doesn't occur under these conditions

Table 6, continued - Corrosion Rules of Thumb

Form of Corrosion	Influencing Factors	Material Characteristic	Potential for Corrosion
Crevice Corrosion	Stagnation of contaminants due to poor fluid flow results in excessive ions available to precipitate corrosion reactions	Small gaps between adjacent components are present where ions can accumulate. Gaps can be caused by inside corners, fasteners, gaskets (not fully in contact with surface), joints, debris buildup, and scale	Crevice corrosion can potentially occur under these conditions
		No gaps are present and joints are welded	Crevice corrosion will not occur
		Is the material a noble metal	Crevice corrosion will not occur
		Does the material have a passive surface	Passive metals are susceptible to crevice corrosion and must be carefully selected based upon specific alloy and environment
Pitting Corrosion	Surface finish including flaws and cracks, stagnant fluids, ionic potential of the electrolyte	Is the material a noble metal	Pitting corrosion will not occur
		Does the material have a passive surface	Passive metals are susceptible to pitting corrosion and must be carefully selected based upon specific alloy and environment
		Is the material oriented in a vertical or horizontal fashion	In stagnant conditions pits are more likely to grow downwards on horizontal surfaces and are less frequent on vertical surfaces. Rarely do they grow upwards. on horizontal surfaces

Table 6, continued - Corrosion Rules of Thumb

Form of Corrosion	Influencing Factors	Material Characteristic	Potential for Corrosion
Intergranular Corrosion	Alloying content, impurities within the metal, heat treatment, welding effects, 2nd phase precipitation products on grain boundaries	2000, 5000 series aluminum alloys	Susceptible to intergranular corrosion
		Austenitic stainless steels	Susceptible to intergranular corrosion
		Endgrains	Susceptible to intergranular corrosion
		Chromium depletion zones adjacent to welds	Susceptible to intergranular corrosion
		Anything with precipitated phases at grain boundaries	Susceptible to intergranular corrosion
		Nickel alloys containing chromium and molybdenum , low carbon content stainless steels, addition of columbium or tantalum to stainless steels	Resistant to intergranular corrosion
Selective Leaching	Exposure to an aqueous solution containing chlorine or other ions, heat treatment, alloy composition, welding	Cast Iron	Highly susceptible
		Copper alloys with a high zinc content (brass)	Highly susceptible
		Aluminum and silicon bronzes	Highly susceptible
		High carbon steels	Highly susceptible
		High nickel alloys	Highly susceptible
		Red brass (less than 15% zinc)	Resistant
		Adding Sn, Sb, As, or P to brass	Resistant
		Malleable or nodular (white) cast iron	Resistant

Table 6, continued - Corrosion Rules of Thumb

Form of Corrosion	Influencing Factors	Material Characteristic	Potential for Corrosion
Erosion Corrosion	Turbulent flow, fluid velocity, density, angle of impact, cavitation	Hardness	Hard metals resistant
		Sharp bends in piping	Susceptible
		Impingement of fluid on impellors, propellers, heat exchanger tubing	Susceptible
		Surface finish	Smooth surfaces are more resistant
		Alloys with protective passive layers	Susceptible
		Alloys with protective hard oxide layers e.g. titanium with TiO_2	Resistant
		High nickel steel alloys	Resistant
		High silicon cast irons	Resistant
Stress Corrosion	Tensile stress (applied mechanical or thermal, residual)	Titanium alloys with Nb, Mo, and V	Improved resistance
		High strength alloys by heat treatment or mechanical hardening	Susceptible
		Iron alloys with nickel	Susceptible if Ni is less than 9%
		Iron alloys with carbon	Susceptible if C is less than .12%
		Austenitic stainless steels	Susceptible
		Lower strength steels	More resistant than higher strength steels
		2000, 7000 series aluminum alloys	Susceptible
		In general, any alloy with protective oxide layers including titanium, copper, zirconium, and magnesium	Susceptible
		Aluminum alloys with less than 4% magnesium	Resistant

Table 6, continued - Corrosion Rules of Thumb

Form of Corrosion	Influencing Factors	Material Characteristic	Potential for Corrosion
Hydrogen Damage	High temperature moist environments, electrolysis, hydrogen evolved form other corrosion mechanisms	High strength steels	Susceptible
		Copper	Susceptible
		Aluminum	Susceptible
		Nickel alloys	Susceptible
		Titanium alloys	Susceptible
		Low strength steels	Less susceptible
		Void free steels	Less susceptible
Corrosion Fatigue	Cyclic load	Same as SCC	Same as SCC
Fretting Corrosion	Vibratory movement between adjacent loaded components	Mating surfaces of concern are aluminum on cast iron, aluminum on stainless steel, hard tool steel on stainless steel, chrome plate on chrome plate, other	Susceptible
		Hard surfaces adjacent to each other such as hard steel on hard steel, steel on rubber gasket	Resistant
Filiform Corrosion	Water permeable organic coatings or edges of alloys coated with metallic coatings exposed to high humidity	Steel, magnesium, aluminum	Susceptible

2.2.3.1 Modifying Design/Performance Requirements

Some materials susceptibilities to particular corrosion forms, such as pitting, intergranular/exfoliation, and selective leaching, are highly dependent upon alloying content and/or heat treatment. A small change in alloying content and/or heat treatment may increase corrosion resistance without significantly degrading other property values. For situations where the material candidate(s) meet or exceed the design's performance requirements yet fall short of the desired corrosion resistance, it may be necessary to select a material similar to one initially under consideration. The old candidate in this case could be eliminated and replaced with a material with a slightly different elemental composition or heat treatment. However, the new candidate must be evaluated for all properties and thus must start back at the beginning of the traditional material selection process.

If during the analysis the final candidate is rejected, the design must be re-evaluated and/or alternate candidate materials added into the selection process. If the design can be modified, the candidates should be put back into the pool for re-evaluation to determine if they now might meet the new requirements. If the design cannot be changed, alternate materials may be identified and evaluated as appropriate.

2.2.4   Step 4: Select Corrosion Prevention and Control (CPAC) Methods

The next step in the process shown in Figure 8 is to select the appropriate corrosion prevention and control (CPAC) methods. This can often be even more daunting than selecting the actual material of construction. Some materials require no CPAC methods at all since they possess surface characteristics that make them resistant to corrosion. Stainless steels are a good example of this. However, most metals (and some other materials) need some mechanism to protect them from the corrosivity of their operating environment. Moreover, in many cases multiple CPAC measures may be needed to provide adequate corrosion resistance. A good example is aluminum, which typically is first subjected to a conversion coating and later primed and topcoated. In this case the three different coatings together provide the necessary barrier needed to prevent corrosion.

2.2.4.1 CPAC Strategies

There are several strategies that can be employed to protect a metallic material from corrosion if and when necessary. A global view of these strategies is presented in Figure 12.

One such strategy, as shown before with the discussion on coatings for aluminum, is to construct a barrier to prevent the corrosive environment from contacting the surface. Effective barriers include coatings, surface treatments, and corrosion preventive compounds (CPCs) such as greases. Another strategy is to modify the environment itself. Now obviously this won't work when a structure is exposed to the elements themselves, but corrosion can also happen inside a structure or system, especially if it is totally enclosed. A good example is a heating plant where steam is circulated from the boiler to heat exchangers. The operational environment within this type of enclosed system contains water, which certainly will be laden with minerals and other contaminants that can initiate corrosion reactions. In these situations a chemical substance known as a corrosion inhibitor can be mixed with the fluid to reduce the corrosivity of the environment. Corrosion can also be controlled by inducing electrical current into the structure

being protected. This has the effect of impeding the electrochemical processes responsible for corrosion. Finally, good maintenance and cleaning practices will prolong corrosion resistance.

A smart approach to corrosion will provide a proper balance of all mitigation strategies in designing, building, operating, and sustaining systems

| "Designed-in" Resistance
• Corrosion-resistant materials
• 'Corrosion-smart' designs | CPAC Methods | Planned Corrosion Maintenance | Repair or Replace |

Higher upfront (acquisition) costs
Less maintenance/repair required
Lower life cycle costs
Longer service life
Higher reliability
Higher readiness
Lower risk
Extending system life is
 easier to accomplish

All strategies are needed for success, but the leftmost balance possible is best for maximizing system life cycle

Lower upfront (acquisition) costs
More maintenance/repair required
Much higher life cycle costs
Shorter service life
Lower reliability
Lower readiness
Higher risk
Extending system life is
more difficult to accomplish

Figure 12   Material Property Needs are Derived from System Performance Requirements

Figure 13   Corrosion Prevention and Control Methods

2.2.4.2   Important Considerations When Selecting CPAC Methods

Figure 13 identifies the methods used to perform corrosion prevention and control. The bottom half of the figure denotes the specific materials employed to control corrosion. The following sections provide additional details on some of these.

Coatings/Primers: Coating systems including primers and topcoats are used extensively for corrosion protection. Basically, if the component is going to be employed in an environment that is corrosive to the material it is constructed from, then a coating should be used. Selection of the coating system depends upon the compatibility with the base materials, the accessibility of the component, the quality of the surface finish required, and the operating environment including all variables as previously shown in Figure 10. In the case of inaccessible areas, a more robust or longer lasting coating system should be used.

When selecting coatings an important consideration is that more durable ones typically come at a higher cost but offer the promise of a longer life with reduced maintenance. However, in many cases choosing the most expensive technique, even if it promises the best performance, may be unaffordable. If the component or system being designed can be easily repainted, then a less expensive and poorer performing coating may suffice. On the other hand, if the component or system is difficult to repaint, either through inaccessibility or by operational needs that preclude taking the item from service, then a better performing coating system is needed.

A final consideration is that some classes of materials might receive additional protection from a surface treatment or metallic coating that's applied prior to the primer/topcoat layers. For example, aluminum structures are often treated with an Alodine™[1] conversion coating prior to being primed and top-coated. Similarly, steel alloys are sometimes galvanized. The use of surface treatments or metallic coatings along with the subsequent application of primer and topcoat layers provides the corrosion resistance needed to protect the system or component while in service. Specific functional requirements, such as low observability or camouflage, may dictate even more layers within the system. The important thing to note is that the coating layers must be compatible with each other and also with the metal structure or component being protected.

Inhibitors: Inhibitors can be used as additives to primers used in coating systems, corrosion preventive compounds, sealants, or they can be substances added to a system as preventive maintenance practices. The use of inhibitors for preventive maintenance is usually seen in closed systems such as pipelines and boilers. They can be used in some open systems, such as cooling towers, but precautions must be taken to prevent environmental contamination. Selection of inhibitors will depend upon the application, the base materials, and the environmental conditions.

CPCs: Corrosion preventive compounds (CPCs), also called corrosion protection compounds, or corrosion preventative compounds; are compounds that are primarily used for temporary protection of accessible areas exposed to highly corrosive environments. They come in the form of oil-based, waxy, or hard films that can be wiped or sprayed onto components. Like other CPC measures, the selection will be based upon the base materials, the operating conditions, and the component's accessibility.

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[1] Alodine is a registered trademark of Amchem Products, Inc.

Cathodic Protection: Another approach for reducing corrosion is to employ mechanisms that can modify the electrochemical processes that consume materials. Cathodic protection, either through the use of sacrificial anodes or electronic impressed current devices, can convert a material that normally will corrode quite readily into a material that resists corrosion. This approach works very well for protecting fixed assets, such as steel structures, pipelines, and buried tanks.

Maintenance Practices: A final measure for reducing corrosion involves maintenance practices. Routine cleaning can significantly reduce the instances of corrosion, but so too can the reapplication of coatings and corrosion preventive compounds. Removing the corrosive substances and other debris while also ensuring the integrity of the protective barrier is one of the most effective ways to reduce the severity of corrosion.

2.2.4.3   Selecting Corrosion Prevention and Control Methods

There are many other important considerations when selecting corrosion prevention and control methods. These considerations are based on the potential corrosion failure modes, application or design features, anticipated environments and candidate materials. Tables 10 – 13 present a directory intended to help guide the selection of corrosion protection and control methods by illuminating related issues that should be considered given potential corrosion failure modes, application or design features, anticipated environments, and/or candidate materials.

Table 7 lists the main forms of corrosion and are matched up with the primary CPAC methods. To use this table, find the relevant form of corrosion and look across the row. A "Y" indicates that is a good method to use to prevent or mitigate this form of corrosion. A "C" indicates that the CPAC method should be used with caution, and is usually accompanied with a footnote that highlights an important consideration. An "O" indicates that other CPAC methods are typically recommended over the one in consideration as it may not be suitable to prevent that particular form of corrosion. Footnotes highlight important considerations for the CPAC method that is paired with the particular form of corrosion.

Table 8 lists generic application and/or design features, which are matched up with the primary CPAC methods. Any features listed in the table that are common to the design/application under consideration should be checked to find suitable CPAC methods. The same notation scheme as Table 7 is used, with footnotes highlighting important considerations.

Table 9 lists generic environments, which are matched up with the primary CPAC methods. The environments that are anticipated for the application in consideration should be checked to find suitable CPAC methods. The same notation scheme as Table 7 is used, with footnotes highlighting important considerations.

Finally, Table 10 lists generic material classes, which are matched up with the primary CPAC methods. Find the metal class which correspond to each candidate material and check for suitable CPAC methods. The same notation scheme as Table 7 is used, with footnotes highlighting important considerations.

Table 7   Directory of Important Considerations for Selecting CPACs Based on the Potential Corrosion Failure Mode

Forms of Corrosion	Coatings	CPCs[i]	Conversion Coatings	Cathodic/Anodic Protection	Mechanical Working (e.g. Shot Peening, LST)	Inhibitors[iii]	Sealants/Gaskets	Design	Material Selection	Preventive Maintenance[iv]
Uniform	Y	C[i]	Y	Y	O	Y	O	Y[ii]	Y	Y
Galvanic	C[v]	C[i]	O	C[vi]	O	C[vii]	Y[viii]	Y	Y	O
Crevice	Y	Y[i]	O	C[ix]	O	Y	Y	Y	Y	Y[x]
Pitting	C[xi,xii]	C[i]	C[xi,xii]	Y	O	Y	O	O	Y	Y[xiii]
Intergranular (IGC)	O	O	O	O	O	Y	O	O	Y[xiv]	O
Selective Leaching	Y[xv]	C[i]	O	Y	O	Y	O	O	Y	O
Erosion	Y[xvi]	O	O	O	C[xvii]	Y	O	Y	Y	O
SCC	C[xviii]	C[xviii]	C[xviii]	O	Y	Y	O	Y[xix]	Y	Y[xx]
Corrosion Fatigue	C[xviii]	C[xviii]	C[xviii]	O	Y	Y	O	Y[xix]	Y	Y[xx]
Hydrogen Damage	Y[xv]	C[i]	O	O	O	Y	O	Y[xix]	Y	Y[xx]
Fretting	Y[xvi]	C[xxi]	O	O	Y				Y	

Y   good CPAC method
C   use with caution
N   Generally not recommended
O   Other methods recommended
Green background indicates preferred method

i   Generally used as a temporary CPAC method, but should be reapplied on a regular basis to maintain corrosion protection
ii   Design materials with greater thickness if possible
iii   Inhibitors are often used in conjunction with other CPAC Methods (e.g. coatings) and in many cases this is recommended
iv   Use in conjunction with other CPAC methods
v   Coatings can be used to electrically isolate the anodic material, but flaws in the coating may accelerate galvanic corrosion
vi   Sacrificial anodes may be used if they are more anodic than the other materials in the system
vii   Inhibitors may only reduce the rate of galvanic corrosion
viii   Sealant or gasket must electrically isolate coupled metals to be effective
ix   May inhibit corrosion in some instances, but sealants and CPCs are recommended
x   Clean out crevice on a regular basis, and reapply coatings/CPCs/Sealants where applicable
xi   Coatings (especially cladding) can effectively prevent pitting, but they must be applied properly and inspected periodically
xii   Scratches/flaws in the coating can result in an increased threat of pitting
xiii   Periodic inspection of coatings/material surface is important in monitoring for pitting
xiv   Contamination during processing can lead to IGC, which is very material sensitive; thus material selection and prescribed processing can reduce instances of IGC
xv   Barrier coatings are recommended
xvi   Coatings that increase surface hardness are recommended
xvii   May increase surface hardness which helps resist erosion
xviii   Coatings may help inhibit initiation of a stress corrosion crack
xix   Design structures to reduce stresses
xx   Material should be inspected for cracks on a regular basis
xxi   Lubricants/greases should be used in systems with moving parts

Table 8   Directory of Important Considerations for Selecting CPACs Based on the Design/Application Features

Application/Design		Coatings	CPCs[i]	Conversion Coatings	Cathodic/Anodic Protection	Mechanical Working (e.g. Shot Peening, LST)	Inhibitors[iii]	Sealants/Gaskets	Design	Material Selection	Preventive Maintenance[iv]
	Closed System	Y	Y	Y	Y	Y	Y	Y		Y	
	Open System	Y	Y	Y	Y	Y	C[xxii]	Y		Y	
	Thin metal component	C[xxiii]	Y	O	C[xxiv]	O	Y			Y	
	Inaccessible for maintenance	C[xxv]	O	C[xxvii]	C[xxvi]	Y	Y		Y	Y	O
	Accessible for maintenance	Y	Y	Y	C[xxviii]	Y	Y			Y	Y
	Wear surface	C[xxix]	O	Y	Y	Y	C[xxx]			Y	
	Large component/structure	Y	O	C[xxxii]	Y[xxxi]	C[xxxii]	C[xxxiii]			Y	
	Small component/structure	C[xxxiv]	Y	C[xxxiv]	Y	Y	Y			Y	
	Weight sensitive application	C[xxxv]	Y	C[xxxvi]	O	Y	Y		Y	Y	Y

Y   good CPAC method
C   use with caution
N   Generally not recommended
O   Other methods recommended

xxii   Requires constant reapplication of inhibitors
xxiii   ensure there is not a CTE mismatch; apply thin coating to avoid spalling due to CTE mismatch
xxiv   excessive current can cause embrittlement and/or an accelerated corrosion in the form of alkaline attack and thus accelerated failure
xxv   be sure to select a durable coating if component cannot be repaired easily
xxvi   Sacrificial anodes may have to be replaced periodically
xxvii   conversion coatings may require periodic repair
xxviii   passive CP anodes must be replaced periodically, but ICCP is OK
xxix   consider a hard coating that is wear resistant
xxx   Organic inhibitors are suitable for wear surfaces, but precipitation inhibitors are not
xxxi   while feasible, large structures are costly to protect using ICCP
xxxii   may not practical for components with large surface areas
xxxiii   may want to incorporate inhibitors in wash/rinse water or paint/coating
xxxiv   If small enough coating may change dimensions of small part; CTE mismatch may distort component
xxxv   most coatings are lightweight, but some, especially metallic coatings/claddings, can add a non-negligible amount of weight
xxxvi   depending on the thickness and surface area covered, conversion coatings may not be entirely negligible

Table 9   Directory of Important Considerations for Selecting CPAC Methods
Based on the Anticipated Environment

Environment	Coatings	CPCs[i]	Conversion Coatings	Cathodic/Anodic Protection	Mechanical Working (e.g. Shot Peening, LST)	Inhibitors[iii]	Sealants/Gaskets	Design	Material Selection	Preventive Maintenance[iv]
Subject to high temperatures	C[xxxvii]		Y	Y	Y	C[xxxviii]	C[xxxix]		Y	
Subject to very cold temperatures	C[xli]		Y	Y		Y	C[xlii]		Y	
High velocity flowing fluid	C[xliii]	O		Y		C[xliv]	Y		Y	
Atmospheric	Y	Y	Y	O[xlv]		Y	Y		Y	Y
Immersed	Y	O		Y		Y	Y		Y	
Soil environment	Y	O		Y			Y		Y	

Y   Good CPAC method
C   Use with caution
N   Generally not recommended
O   Other methods recommended
Green background indicates preferred method

xxxvii   few organic coatings (e.g. phenolics) available for high temperature service
xxxviii   some inhibitors (e.g. organophosphates, amine-based compounds) may be sensitive to high temperatures
xxxix   some gasket materials break down or creep at high temperatures
xli   organic coatings may not perform well below the glass transition temperature (Tg)
xlii   some gasket materials become brittle at low temperatures (below Tg)
xliii   harder coatings are recommended especially if impingement is a concern
xliv   precipitation inhibitors may be worn off
xlv   cannot be used to protect in atmospheric environments

Table 10   Directory of Important Considerations for Selecting CPACs Based on the Candidate Material

Material		Coatings	CPCs[i]	Conversion Coatings	Cathodic/Anodic Protection	Mechanical Working (e.g. Shot Peening, LST)	Inhibitors[iii]	Sealants/Gaskets	Design	Material Selection	Preventive Maintenance[iv]
	Steel	Y			Y					Y[liii]	
	Titanium				Y					Y[liii]	
	Zinc	Y			O[xlvi]					Y[liii]	
	Copper	Y			O[xlvi]					Y[liii]	Y
	Cadmium				O[xlvi]					Y[liii]	
	Magnesium	Y	Y	O	O[xlvi]	O[xlviii]	Y	Y	Y[xlix]	Y[liii]	
	Aluminum	Y		Y[l]	C[xlvii, lii]		Y		Y[li]	Y[liii]	
	Lead				C[xlvii]					Y[liii]	
	Nickel-based alloys						Y			Y[liii]	

Y   Good CPAC method
C   Use with caution
N   Generally not recommended
O   Other methods recommended
Green background indicates preferred method

xlvi   Anodic protection cannot be used
xlvii   excessive current can cause embrittlement and/or an acceleration of corrosion from alkaline attack
xlviii   susceptible to contamination which leads to poor corrosion performance
xlix   Drainage-friendly designs to keep moisture out will help reduce corrosion
l   anodization is a particularly good method of protection
li   Use high surface area ratio aluminum to cathodic metal, if aluminum is electrically connected with another metal
lii   Sacrificial anodes and anodic protection can be used
liii   select specific alloy to tailor corrosion resistance depending on environmental conditions, application, and design considerations

2.2.4.4   Strategic Methods to Perform Corrosion Prevention and Control

Design, maintenance, and material selection can be strategically used to minimize the extent to which a material, component or system corrodes during its lifetime. Simple elements incorporated into a design can lessen the risk of corrosion. For example, allowing for drainage of water that otherwise might become trapped can effectively reduce corrosion problems. Similarly, employing seals to preclude water from entering a component or system will provide similar results. Another effective way to minimize corrosion is to use gaskets to electrically insulate two dissimilar metals, thus eliminating the possibility of galvanic coupling between adjacent components. Employing a maintenance schedule where a vehicle or structure is periodically cleaned to remove salt or debris buildup will help reduce corrosion. In addition, regularly touching up protective coatings or reapplying CPCs will help reduce instances of corrosion. Perhaps the most important way to minimize corrosion from occurring in the first place is to make appropriate material selection decisions upfront by carefully considering the application, environment, and potential corrosion problems that might occur. Selecting the appropriate materials and associated corrosion prevention and control practices can reduce maintenance costs and system downtime over the life-cycle of a system.

2.2.5   Step 5: Assess Other Factors

The fifth step in the process shown in Figure 8 is to assess other factors that may influence the final decision. Selecting the best material among the chosen candidates is based not only upon inherent corrosion resistance and performance, but on a number of other factors including availability, maintainability, and cost. These factors all contribute to a system's operational and cost effectiveness, as depicted in Figure 14, and since they are traditionally covered in any material selection analysis, the process described here will not cover them in-depth.
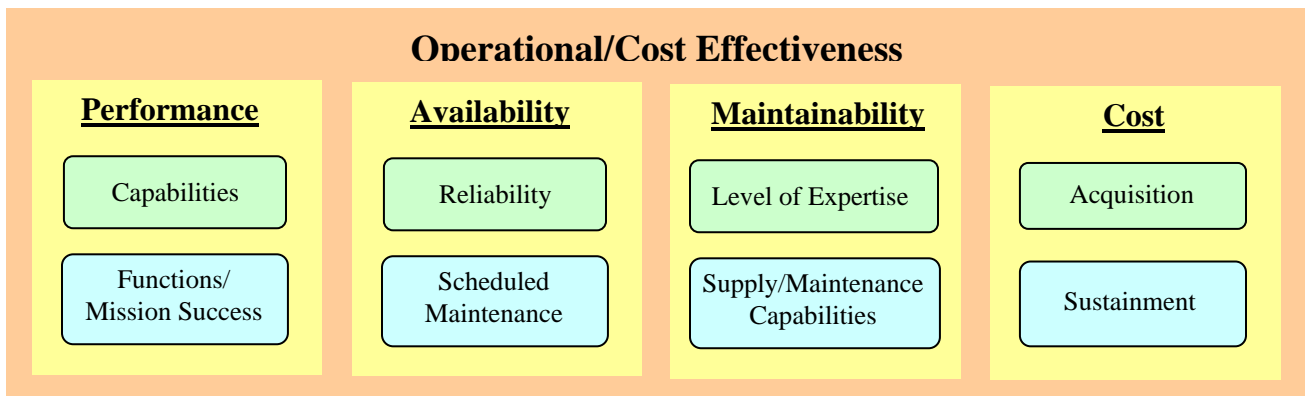
Figure 14   Operational Effectiveness

Before conducting a cost analysis one must first determine the life expectancy of the system or component being designed. The strategies employed while conducting the analysis differ depending upon whether the system or component will have a short or long life and whether it is a critical or non-critical item. Corrosion may be tolerated to a greater extent in short-lived or non-critical applications. In these situations the cheapest remaining material candidate and CPAC method might be appropriate. Conversely, if the application being designed is critical and failure cannot be tolerated, or if it is a component that is expected to remain in-service for a

considerable length of time, then far more thought and effort must be given to selecting both the material and the CPAC method.

The two primary cost factors that affect materials selection are the acquisition and sustainment costs. The acquisition costs are straightforward as they are due to procuring the raw materials and processing/manufacturing them into the component/system. Sustainment costs are due to routine preventative maintenance and repair actions. The cost for routine maintenance can be projected from a combination of past experience to determine labor times, and the cost of preventive maintenance materials chosen for the new system. Repair costs can be estimated for different materials, but corrosion failure rates cannot be predicted with accuracy for most components. Therefore, the cost analysis will most likely be the sum of the acquisition costs and routine maintenance costs. One should also note, however, that materials with higher susceptibilities to corrosion will be more likely to fail or will require extensive maintenance actions. Figure 15 represents the acquisition and sustainment costs of two notional materials systems over time. System A represents the life-cycle costs of a system developed using materials and CPAC methods that together are more susceptible to corrosion than System B, which uses materials and CPAC methods that are more resistant. The acquisition costs for System B are greater but so too is its life span, assuming the two systems employ the same level of attention to preventive maintenance. Extending the life of System A, after it has been fielded, to be comparable to System B's would be a costly proposition.
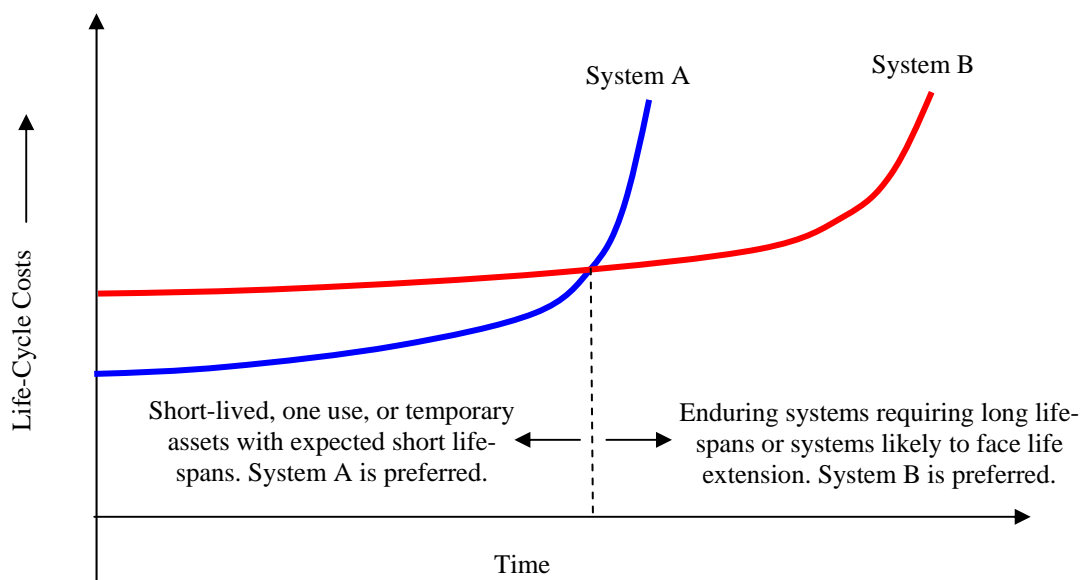
Figure 15   Acquisition and Sustainment Costs of Two Differently Chosen Materials Systems

2.2.6   Step 6: Down-select Final Material & CPAC Method

As shown in Figure 8, the final step is to down-select the final candidate material (if multiple materials are being considered) and CPAC method. At this point a thorough analysis of the initial candidates has been completed, and most likely, several of the more problematic candidates have already been rejected. The final selection will depend upon the relative

importance of performance corrosion resistance, availability, maintainability, and cost. If at this point all of the remaining candidate(s) are determined to be unacceptable, then alternate materials need to be chosen.

2.3   Conclusions

For critical applications the best approach for ensuring corrosion resistant designs is to employ the use of trained corrosion specialists or materials engineers to help select the most appropriate materials and corrosion prevention and control practices. However, we realize that for many organizations and designs this may not be feasible. What we have presented here is an approach that designers can use to improve their consideration of corrosion prevention and control during material selection. The approach may seem a bit complicated, but one thing is certain; using it or a similar process will help reduce corrosion and related life-cycle costs.

The US Government, specifically the Departments of Defense and Energy, as well as NASA and other Federal agencies, have funded literally tens of thousands of corrosion-related research projects over the past many decades. Much of the information resulting from this research is available to help reduce performance risk on new acquisition programs. The difficulty with using this information is obtaining it in a timely fashion. Much of it currently resides in paper collections or microfilm, thus restricting the ease at which it can be obtained. Because of the variety of interests of those who conducted this research, it's likely that information exists that is directly relevant to any given application, intended environment, and candidate material. In the absence of using such data, designers should still endeavor to utilize the more general information contained in reference books and handbooks. Doing one's 'homework' to the maximum extent possible will pay dividends later with reduced life-cycle costs and increased readiness rates.

DoD policy now requires program managers to provide evidence that they have planned for corrosion mitigation when they present their procurement strategies before acquisition review panels, such as the Defense Acquisition Board. For those involved with supporting a DoD-related or other Government acquisition program, it makes sense to use the best design practices and information to ensure the customer is delivered a durable system or structure that possesses the lowest life-cycle costs and highest readiness rates possible, maximizing their return on investment, and providing the U.S. taxpayer with the best value for their tax dollar.

Making the final selection decision requires a great degree of engineering judgment. Comparing the material properties of candidate materials to find the best one is a straightforward process. However, determining which one will perform best in a corrosive environment is a far more difficult proposition. The process shown here provides you a 'roadmap' of the essential issues to consider during the analysis. Effectively reaching the correct decisions requires you to consult the literature to get the technical literature. This will provide you with the basis needed to make the correct decisions.

3.0 Environments and Their Affects on Corrosion Processes

The environment plays a major role in the selection of materials for corrosion resistance. Environmental factors that may influence corrosion include the environment's composition, pH level, humidity, wind or water currents, and temperature. These factors exist in the following types of environments, atmospheric, fresh water, saltwater, and soil, which will be discussed in this section. Additional microenvironments, such as specific acid susceptibilities of metals and microorganisms will be covered in Section 6.0 Corrosion Characteristics and Properties of Metals and Section 4.9.6 Microbiological Corrosion respectively.

3.1 Atmospheric Environments

Atmospheric corrosion can vary widely depending on contaminants present, humidity and rainfall, wind and temperature. Extensive atmospheric testing programs have been conducted to compute corrosion rates of metals and to characterize metals' susceptibilities to various forms of corrosion. A typical atmospheric testing rack is shown in Figure 16. Such studies have lead to the broad categorization of environments into rural, urban, industrial, marine, and combinations of them. A general characterization of the four main types is listed in Table 11.

Deviations of corrosion rates within the four categories have lead to a further subcategorization based upon weather and climate. These additional factors influencing corrosion are temperature, humidity and rainfall. The relative corrosion rates for these environments are found in Table 12

Figure 16   Atmospheric Corrosion Test Rack[2]

Table 11   Types of Atmospheric Environments[6]

Atmosphere Type	Description
Rural	- generally the least corrosive - does not contain any significant amounts of pollutants - principal corrodants are oxygen and moisture content
Urban	similar to rural but with sulfur oxides (SO_X) and nitrous oxides (NO_x) from vehicle and domestic fuel emissions.
Industrial	- pollutants of sulfur dioxide, chlorides, phosphates, and nitrates exist from heavy industrial processing facilities - special cases include contaminants of hydrogen sulfide, hydrogen chloride, and chlorine which are highly corrosive to most metals.
Marine	- generally high corrosivity - characterized by chloride particles - deicing salts used in cold weather regions produce an environment similar to marine

Table 12   General Corrosion Rates for Different Atmospheric Environments[3]

Rate of Corrosion	Type of Environment		
High	Tropical	Industrial	Marine
Moderate	Temperate	Suburban	
Low	Arctic	Rural	Inland

3.1.1   Atmospheric Contaminants

The primary sources of atmospheric contaminants come from chlorides in marine locations, and industrial and automobile pollutants. These contaminants deposit onto metal surfaces where they react primarily with oxygen, water, and free electrons producing metal compounds which have varying degrees of solubility; producing varying increased corrosion rates over non-corrosive environments.

The presence of chloride salts in the atmosphere significantly increased the corrosion rates of most metals. In the case of ferrous metals, chloride anions combine with ferrous cations to produce iron chloride. Iron chloride is more soluble than the ferrous hydroxide produced in a benign environment, leading to an increased corrosion rate. Other metals such as copper and zinc produce metal chlorides which are less soluble than ferrous chlorides. These metals therefore experience increased corrosion rates, but not to the extent of ferrous metals. It is notable that deicing salts used on roadways in winter months produce corrosivity in those environments similar to marine atmospheric environments.

Sulfur dioxide (SO_2) and nitrous oxides (NO_x) are found in industrial and urban environments from the burning of fossil fuels. Sulfur dioxide deposited on metal surfaces will react with oxygen and free electrons from the metal surface, producing sulfate ions, as expressed in

Equation 1. The sulfate ions lead to the formation of metal sulfates, which in turn react with water to complete the corrosion process, Equation 2.

$$SO_2 + O_2 + 2e^- \longrightarrow SO_4^{2-}$$

Equation 1

$$FeSO_4 + 2H_2O \longrightarrow FeOOH + SO_4^{2-} + 3H^+ + e^-$$
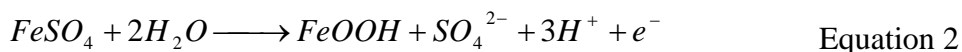
Equation 2

As seen in Equation 2, sulfate ions are again produced in the case of ferrous metals, producing a self-contained corrosion process once sulfur dioxide is present. This process may not occur as readily with other metals nor are most of the metal sulfates produced as soluble as iron sulfate. The presence of nitrous oxides may also increase corrosion rates of metals in a like manner, although they do not deposit on metals as readily as sulfur dioxide.

There are a few additional atmospheric contaminants that are less abundant or may be found in special industrial environments. Hydrogen sulfide is extremely corrosive to most metals. This compound is readily found in oil-refining and petroleum industries. Hydrogen chloride and chlorine gas have been found to produce higher corrosion rates than chloride salt environments. Ammonia, sulfur trioxide, and smoke particles will also increase atmospheric corrosion of most metals. The typical concentrations of these major contaminants are found in Table 13.

Table 13   Typical Concentrations of Several Atmospheric Contaminants[3]

Contaminant	Region	Season	Typical Concentration ($\mu g/m^3$)
Sulfur Dioxide (SO_2)	Industrial	Winter	350
		Summer	100
	Rural	Winter	100
		Summer	40
Sulfur Trioxide (SO_3)	-	-	Approximately 1% of the SO_2 content
Hydrogen Sulfide (H_2S)	Industrial	Spring	1.5-90
	Urban	Spring	0.5-1.7
	Rural	Spring	0.15-0.45
Ammonia (NH_3)	Industrial	-	4.8
	Rural	-	2.1
Chloride (Cl^-, Air Sampled)	Industrial inland	Winter	8.2
		Summer	2.7
	Rural Coastal	Annual (Avg.)	5.4
Chloride (Cl^-, Rainfall Sampled)	Industrial Inland	Winter	7.9
		Summer	2.7
	Rural Coastal	Winter	57 mg/l
		Summer	18 mg/l
Smoke Particles	Industrial	Winter	250
		Summer	100
	Rural	Winter	60
		Summer	15

3.1.2   Humidity and Rainfall

Humidity is also a major factor in determining the corrosion rate of metals, as moisture provides the electrolyte, which is required for corrosion reactions to take place. In general, the corrosion rate increases as humidity increases. The critical level of relative humidity in order for serious corrosion to occur in the absence of other electrolytes is usually taken to be 60%.[3] This critical level of relative humidity may vary depending on the impurities present in the atmosphere. Rainfall can increase or decrease corrosion processes. In areas where stagnant water may accumulate, a localized corrosion cell will most likely be the result. However, rain may also wash corrosive deposits off from metal surfaces, decreasing corrosivity.

3.1.3   Wind

The wind plays a role in the direction and distance atmospheric contaminants are dispersed. The corrosivity of atmospheric environments and therefore general corrosion rates of metals, are related to their distance and proximity to coastal waters and industrial plants.

3.1.4   Temperature

Temperature can have a significant effect on the corrosion of metals, with increased rates of corrosion as temperature is increased. Temperature may also affect the form of attack that the corrosion takes on; for example, changing the temperature may change the corrosion mechanism from uniform to pitting. It can also evaporate condensed moisture on metallic surfaces leaving behind corrosive contaminants. High temperatures can produce a form of corrosion where gas becomes the electrolyte as opposed to a liquid medium. This form, appropriately named "high temperature corrosion," is covered in Section 4.9.4.

3.1.5   Atmospheric Corrosivity Algorithms

There has been some corrosion algorithms developed to compute corrosivity values for given environmental conditions. A couple methods are described here which include the Pacer Lime Program sponsored by the USAF, and ISO Standard 9223. These methods however, use average values to compute their corrosivity indices and only provide a general characterization of atmospheric corrosivity for various environments.

An atmospheric corrosivity severity classification system was developed by Summit and Fink under the Pacer Lime Program to provide management information for the maintenance of aircraft [4] Measurements of environmental conditions were made at numerous USAF bases to compute a corrosivity algorithm. Environmental conditions considered as part of the algorithm are distance to coastal waters, SO_2 content, total suspended particles, humidity, and rainfall. A severity index was created and used to schedule the frequency of various preventive maintenance tasks on aircraft. The algorithm developed to schedule the frequency of washing aircraft, is shown in Figure 17
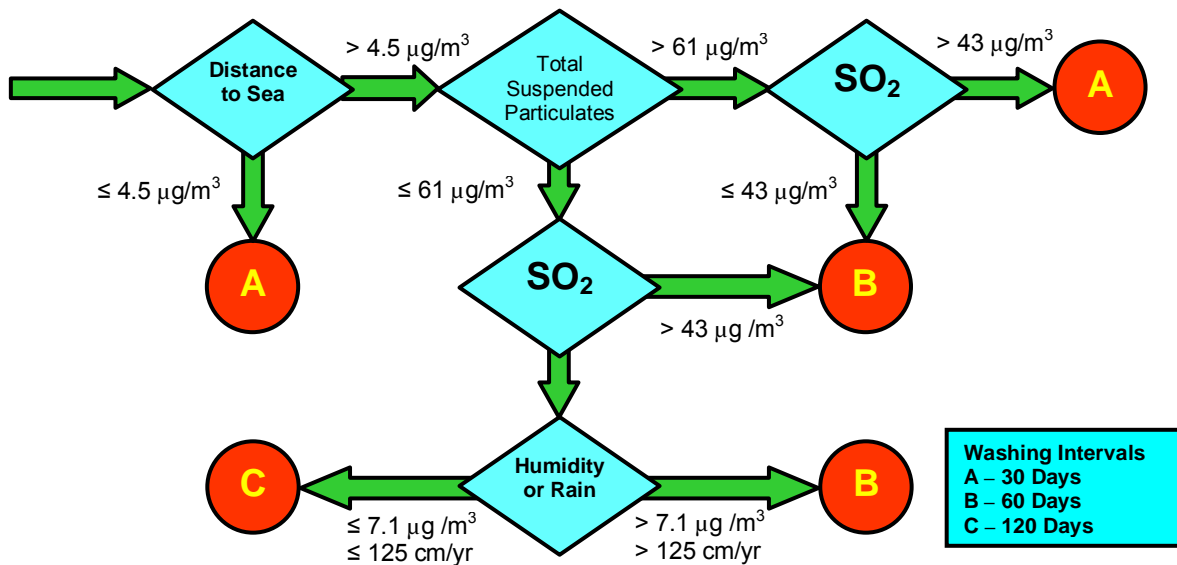
Figure 17   Corrosion Severity Algorithm for Planning an Aircraft Washing Schedule[6]

The ISO 9223 Standard uses the time of wetness and the deposition rates of sulfur dioxide and chlorides to compute an atmospheric corrosivity index.[6] The time of wetness is in units of hours per year, and consists of the time when the relative humidity is >80% and the temperature is >0ºC. The three conditions are divided into five ranges of values used to produce five corrosion categories represented in Table 14.

Table 14   ISO 9223 Corrosion Categories/Rates after One Year Exposure[6]

Corrosion Category	Steel $(g/m^2$-yr)	Copper $(g/m^2$-yr)	Aluminum $(g/m^2$-yr)	Zinc $(g/m^2$-yr)
C_1	≤ 10	≤ 0.9	negligible	≤ 0.7
C_2	11 – 200	0.9 – 5	≤ 0.6	0.7 – 5
C_3	210 – 400	5 – 12	0.6 – 2	5 – 15
C_4	401 – 650	12 – 25	2 – 5	15 – 30
C_5	651 - 1500	25 - 50	5 - 10	30 - 60

3.1.6   Managing Atmospheric Corrosion

General methods to minimize the effects of atmospheric corrosion include the following:

- Proper selection of material for the type of environment and corrosive contaminants present.

- Proper component/system design to limit contaminants and water build-up.

- Use organic and/or metallic coatings and sealants wherever feasible.

- Vapor phase corrosion inhibitors may be used in microenvironments, such as the inside of boilers.

3.2   Water Environments

Factors contributing to the corrosivity of water environments include the composition, pH level, temperature, water velocity, and biological organisms. Water environments are divided into natural or fresh water, and seawater type environments. Fresh waters are used extensively in cooling systems, boiler feed waters, processing of materials and products, washing and drinking waters.

3.2.1   Water Compositions

The composition of water can be quite different, dependent upon the materials and contaminants picked up from the atmosphere during rainfall, the surrounding soil, and man-made pollutants dumped or spilled into waterways. The compounds most responsible for general water corrosivity are dissolved gases and salts. There may additionally be dissolved compounds present in specific areas from pollutants.

The primary dissolved gases affecting corrosion in waters are oxygen and sulfurous gases. Oxygen is by far the biggest concern, as it directly relates to higher corrosion rates for many metals. The concentration of oxygen is greatest at water surfaces and in the presence of algae. Sulfur dioxide and hydrogen sulfide significantly increase corrosivity and are found in waters as a result of pollutants and/or microorganisms. Sulfate reducing bacteria converts sulfates to sulfides. Nitrogen, like in atmospheric environments, is less abundant, but will increase corrosion rates of metals where present.

The ions from dissolved salts mostly responsible for increased water corrosivity are chlorides and sulfates. These ions react with metal cations to produce corrosion reactions. A run down of the most common constituents and ions present in seawater are listed in Table 15. Cations present may reduce corrosion by reacting with available anions. The measure of calcium and magnesium solid precipitates determines the hardness of water. Table 16 represents the general characteristics of some natural waters. A measure of the water's electrical resistivity gives a general indication of corrosivity.

Table 15   Typical Contents and Ions Found in Seawater[5]

Constituent	Content (g/kg of seawater)	Cations	Percent	Anions	Percent
Chloride	19.353	Na^+	1.056	Cl^-	1.898
Sodium	10.76	Mg^{++}	0.127	SO_4^-	0.265
Sulfate	2.712	Ca^{++}	0.040	HCO_3^-	0.014
Magnesium	1.294	K^+	0.038	Br^-	0.0065
Calcium	0.413	Sr^{++}	0.001	F^-	0.0001
Potassium	0.387				
Bicarbonate	0.142	Total	0.262	Total	2.184
Bromide	0.067				
Strontium	0.008				
Boron	0.004				
Fluoride	0.001				

Table 16   Typical Natural Water Analyses[6]

Characteristic	A	B	C	D	E	F	G
pH level	6.3	6.8	7.4	7.5	7.1	8.3	7.1
Chloride (ppm)	5	11	24	21	4	94	149
Sulfate (ppm)	6	20	39	50	17	109	463
Total hardness (ppm)	10	53	120	230	340	70	559
Total dissolved solids (ppm)	33	88	185	332	400	620	1670

A = very soft lake water   C = slightly hard river water   E = hard borehole water
B = moderately soft surface water   D = moderately hard river water   F = slightly hard borehole water with bicarbonate ions
                                                                         G = very hard groundwater

3.2.2   pH Level

The pH level of both natural and seawaters is usually within 4.5 to 8.5. Copper is one metal in which the corrosion rate increases in acidic water. Copper from the corrosion process will then deposit on other materials present producing a greenish stain. The deposition of copper onto aluminum or galvanized metals sets up pitting corrosion.

3.2.3   Temperature

Higher temperatures normally produce increased corrosion rates in water, like other environments. Increased temperatures do decrease oxygen solubility in water. However, warm temperatures will also increase biological growth which can increase oxygen content. And like in any environment, higher temperatures generally speed up corrosion reactions.   The temperature, as well as oxygen content and salinity as a function of ocean depth are depicted in Figure 18   .
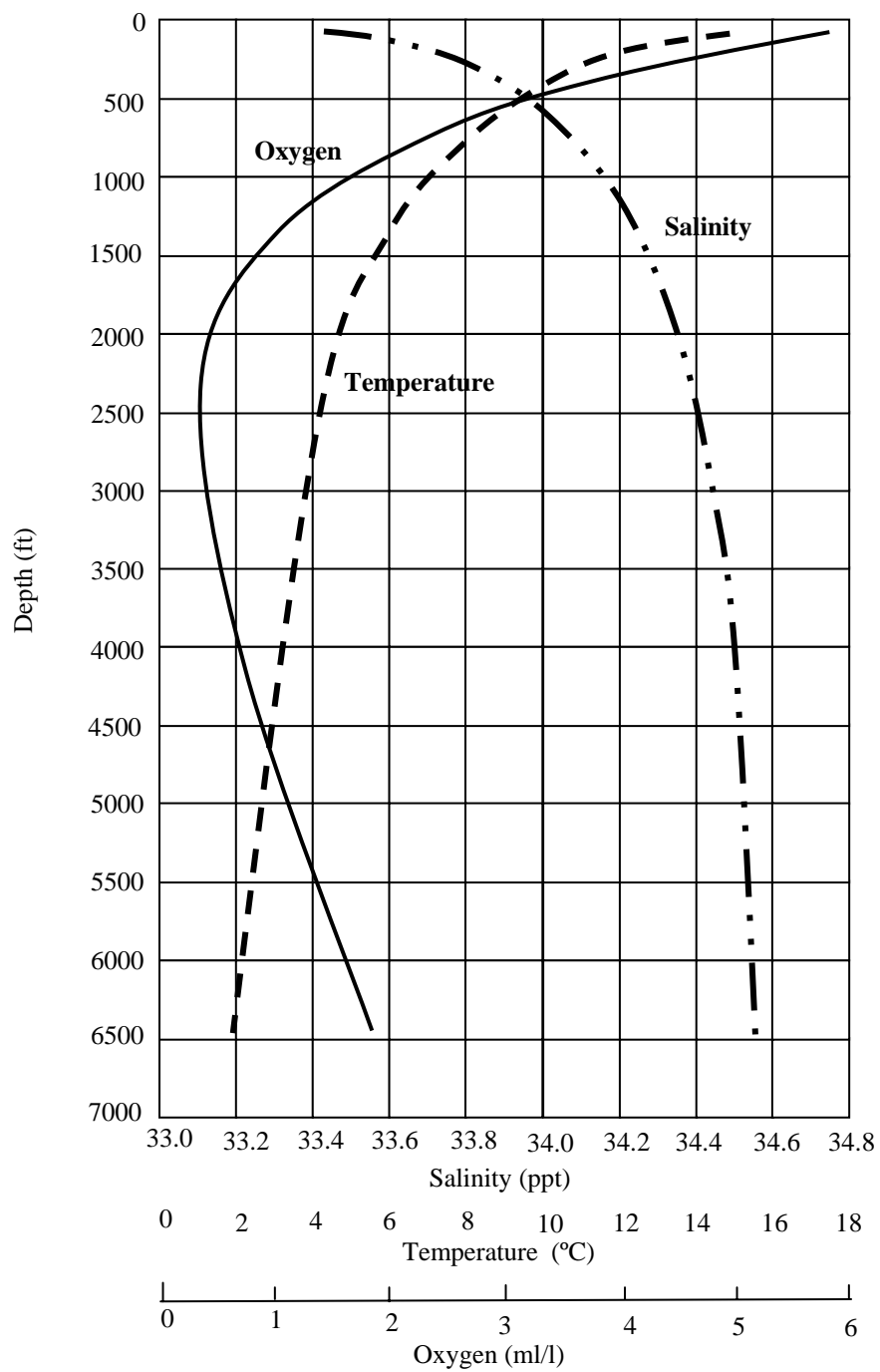
Figure 18   Some Corrosivity Factors as a Function of Depth in the Pacific Ocean
(West of Port Hueneme, California)[5]

3.2.4   Water Velocity and Agitation

The water velocity and agitation may increase or decrease corrosion rates, dependent upon the particular metal. The relative degree of attack on some marine metals is shown in Figure 19. Most metals have a critical velocity, beyond which significant corrosion occurs.

	Flow Condition			
Alloy	**Stagnant (crevice)**	**Quiescent**	**Moderate**	**High Velocity**
Aluminum 2024, 2219, 7178, 7079, 7075, 3003				
2014, 6061, 7002, 5052, 5154, 1100				
5456, 5086, 5083				
90/10 CuNi				
70/30 CuNi				
Monel (Ni-alloy)				
Stainless Steels				
Hastelloy C (Ni-alloy)				

Degree of corrosive attack   None   Little   Moderate   Considerable
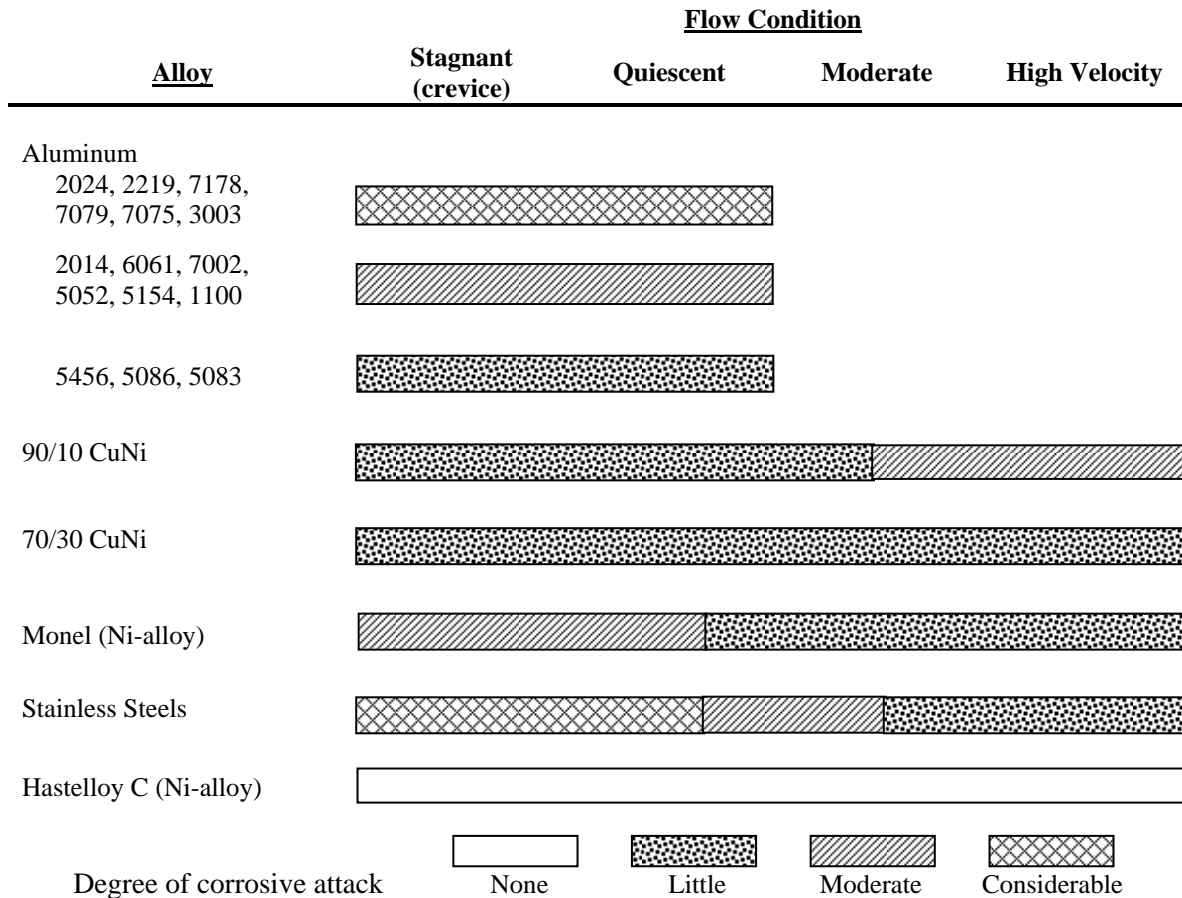
Figure 19   Localized Attack (Crevice and Pitting) of Some Metals in Flowing Seawater[5]

3.2.5   Biological Organisms

All biological organisms, either animals or plants, alter the composition of surrounding water, which may result in increased or decreased corrosion rates. Some organisms merely provide a protective layer, limiting oxygen from reaching the metal's surface. Others increase the oxygen or sulfide content, increasing the corrosive attack on metals. Microorganisms will be discussed further in Section 4.9.6. Figure 20 shows some corrosivity factors and their effect on the uniform corrosion rate of carbon steel in the Pacific Ocean.
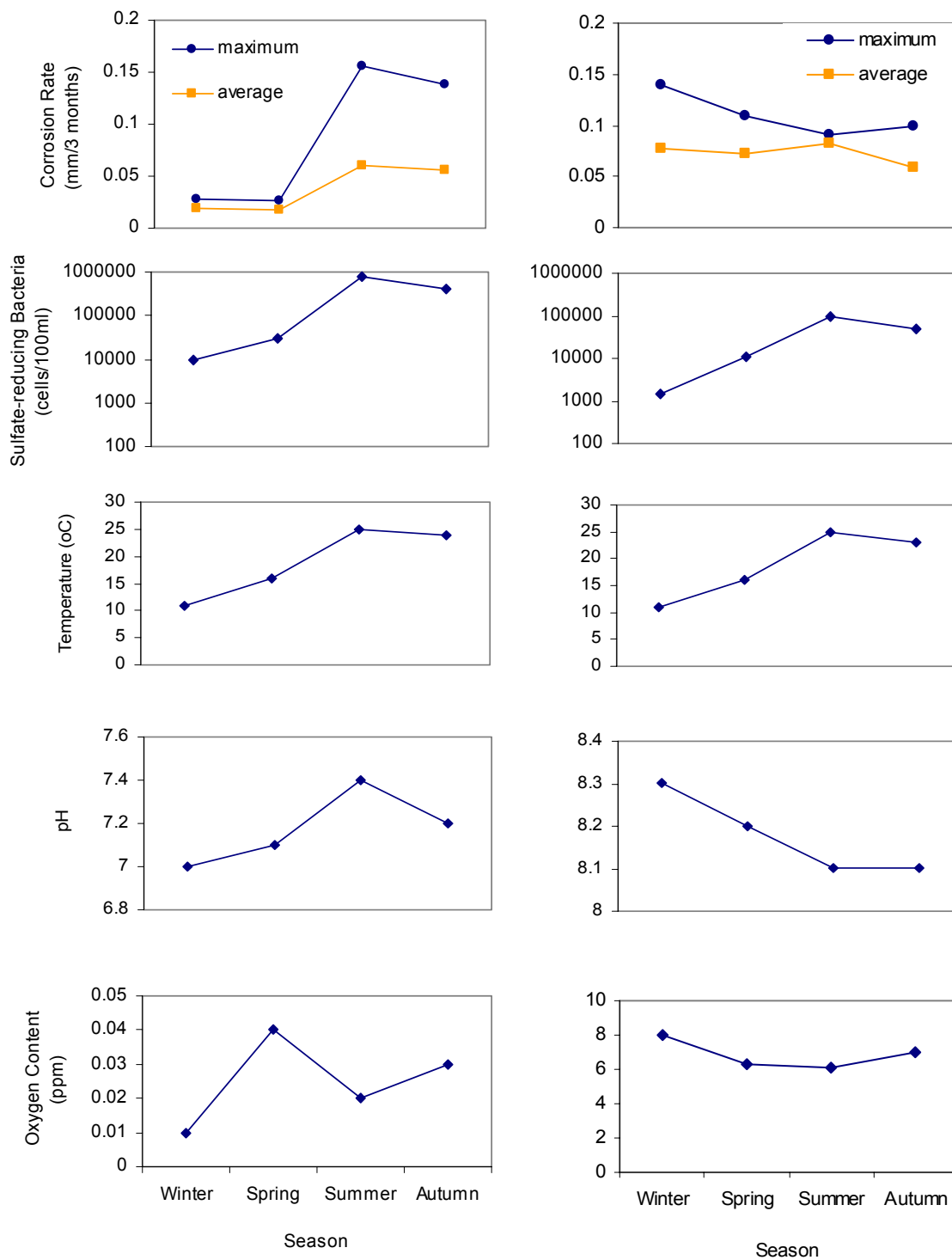
(a)   polluted seawater (Okudokai Harbor)   (b) non-polluted seawater (Kaman Strait)

Figure 20   Factors Affecting the Corrosion of Carbon Steel in the Pacific Ocean[7]

3.2.6   Managing Underwater Corrosion

Methods to limit uniform underwater corrosion include:

- Proper selection and design of materials.

- Specialized underwater paints should be used where feasible (to include formulations for the deterrence of microorganisms.

- Cathodic protection should be used when practical.

- Preventive maintenance to remove microorganisms and other marine animals from surfaces.

3.3   Soil Environments

The corrosivity of soils is affected by water, the degree of aeration, pH level, temperature, salt content, and biological activity. The soil's particle size plays a role in that smaller particle sizes will hold water, and have less oxygen content; while the opposite exists for large particle sizes. Loose soil will also have greater oxygen content. The oxygen content is highest near or at the soil's surface and decreases with increasing depth. Soils normally have pH levels in the range 5 to 8. At these levels, the corrosion rate is not significantly affected. However, acidic soils will increase the rate of attack on most metals, and will affect other factors such as microbiological activity. Salt content affects soils in the same manner as atmospheric and water environments, with the major corrosive species once again being chloride and sulfate ions. Sulfate reducing bacteria is the most detrimental microorganism to metal corrosion. Like the water environment, a measure of the soil's electrical resistivity is a general indication of its corrosiveness. Lower resistivity equates to higher corrosivity. Table 17 lists soil resistivity ratings based upon resistivity. Mappings of soil resistivities are used to determine where to lay underground piping. It is beneficial to route pipelines through soil with like resistivities and ideally, high resistivities. Care must be taken when laying pipelines in the vicinity of other structures, such as railways, to minimize their exposure to stray currents.

Table 17   Soil Corrosivity Ratings[6]

Soil resistivity (Ω -cm)	Corrosivity rating
> 20,000	essentially non-corrosive
10,000 – 20,000	mildly corrosive
5,000 – 10,000	moderately corrosive
3,000 – 5,000	corrosive
1,000 – 3,000	highly corrosive
< 1,000	extremely corrosive

3.3.1 Managing Corrosion in Soil

Methods to limit corrosion in soils include:

- Proper selection and design of materials.

- Metals should be coated where possible. Bituminous coal tar and asphalt dip coatings are effective for under ground piping. Imbedding pipes in concrete has also been used to limit corrosion.

- Cathodic protection should be used where possible.

- Pipes in the vicinity of electric railroad tracks or other similar equipment must be electrically insulated. One method is to coat the piping with hot asphalt followed by a concrete encasement. Organic dielectric coatings have also been developed for this purpose.

4.0   Forms of Corrosion

There are eight major forms of corrosion accounting for the vast majority of corrosion problems observed, along with several lesser seen forms occurring in specific environments. Uniform or general corrosion proceeds independent of the material's microstructure and component design. It is highly dependent upon the environmental conditions and the material's composition, generally occurring at a slow rate. All the remaining forms of corrosion are localized, dependent upon the environments, the components and systems designs, and/or the microstructure of the materials. These forms typically produce higher corrosion rates than uniform corrosion, and in some cases can be quite rapid. Each of the various forms of corrosion should be evaluated for a material and environment when designing new systems. The following sections cover all the forms of corrosion observed with some materials' susceptibilities and general protection schemes for the various forms.

4.1   Uniform Corrosion

Uniform corrosion is a generalized corrosive attack that occurs over a large area on the surface of a material. It is only dependent upon the material's composition and the environment. The result is a thinning of the material until failure occurs. Uniform corrosion rates are fairly predictable, following an exponential relationship as follows.

$$p = At^{-B} \hspace{3cm} \text{Equation 3}$$

where,

      p – corrosion rate
      t – exposure time
      A, B – constants, dependent upon material and environment

The decrease in corrosion rate with time is a direct result of an oxide scale layer forming on the metal's surface, which then deters further corrosion from occurring. There are extreme cases however, where the corrosivity of the environment is severe and prevents an oxide layer from forming. In this case, the corrosion rate will be constant with time. Figure 21 depicts this relationship for uniform corrosion. Equation 3 may be used to predict the long-term corrosion damage from short-term tests. There are some problems with this prediction however. Environments usually change over time so that corrosion rates will deviate from those predicted by the equation. Also, the development of additional forms of corrosion will likely accelerate attack in localized areas.
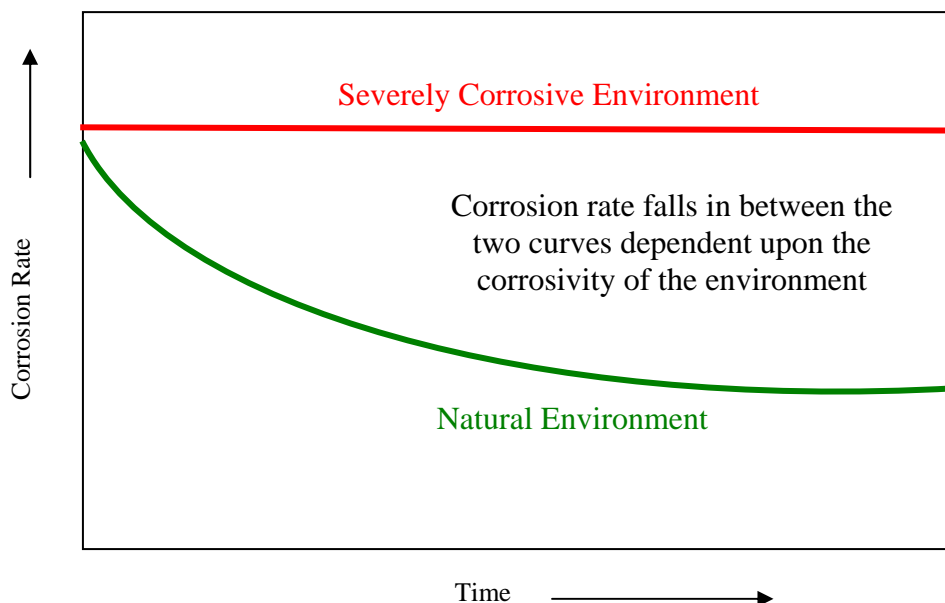
Figure 21   Uniform Corrosion Rates

Uniform corrosion is measured in weight loss or thickness loss and is converted from one to the other using the equation.

$$t = \frac{534w}{\rho A T}$$ Equation 4

where

        t – thickness loss in mils/yr

        w – weight loss in mg.

        ρ – density in g/cm^3

        A – area of exposure in inches^2

        T – exposure time in hrs.

4.1.1   Metal Susceptibilities to Uniform Corrosion

Magnesium and low alloy ferrous alloys are by far the most susceptible metals to uniform corrosion as shown in Figure 22. Additional metal classes, not addressed in the figure, normally have negligible uniform atmospheric corrosion rates. For the susceptible metals, increased alloying with specific elements can increase uniform corrosion resistance. Alloying for general corrosion resistance of the different metal classes is covered in Section 6.0,

Corrosion Characteristics and Properties of Metals. Alloying should also consider the environmental composition and degree of corrosivity. The relative uniform corrosion susceptibilities of a steel piling exposed to marine environments are shown in Figure 23.
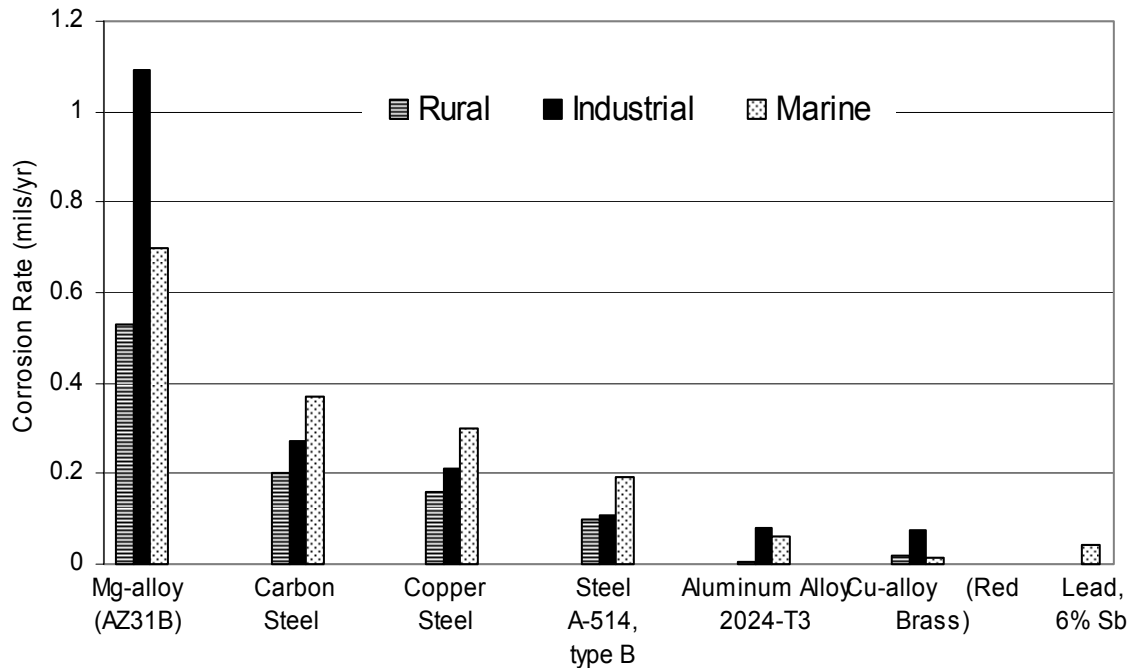
Figure 22   Atmospheric Corrosion Rates of Various Metals[8]

Splash Zone – above high tide
Tidal Zone – below high tide and above low tide
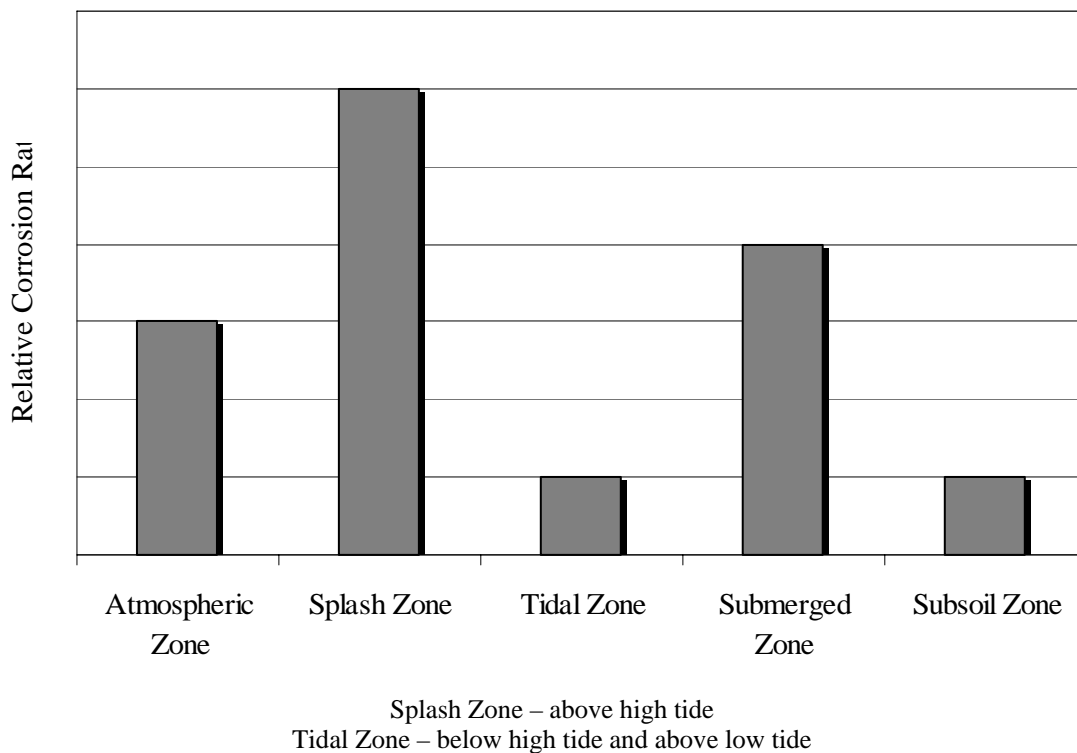
Figure 23   Relative Uniform Corrosion Rates of a Steel Piling in Marine Environments[58]

4.1.2   Managing Uniform Corrosion

The selection of materials for uniform corrosion resistance should simply take into consideration the susceptibility of the metal to the type of environment that will be encountered. Organic or metallic coatings should be used wherever feasible. When coatings are not used, surface treatments that artificially produce the metal oxide layer prior to exposure will result in a more uniform oxide layer and the thickness may be controlled. There are also surface treatments where additional elements are incorporated for corrosion resistance, such as chromium. Also, vapor phase inhibitors may be used in such applications as boilers to combat corrosive elements and adjust the pH level of the environment.

4.2   Galvanic Corrosion

Galvanic corrosion occurs when two metals having different electrical potentials (dissimilar metals) are electrically connected, either through physically touching each other or through an electrically conducting medium, such as an electrolyte. Systems meeting these requirements essentially form an electrochemical cell which will conduct electricity. The induced electrical current can then attract electrons away from one of the metals, which thus acts as the anode in the electrochemical cell. This usually results in acceleration of the rate of corrosion of the anode. The opposing metal, the cathode, will consequently receive a boost in its resistance to corrosion, since it can supply any imminent corrosion reactions with electrons from an external source. Galvanic corrosion is usually observed to be greatest near the surface where the two metals are in contact. Figure 24 shows galvanic corrosion on a metal component near a dissimilar metal fastener.
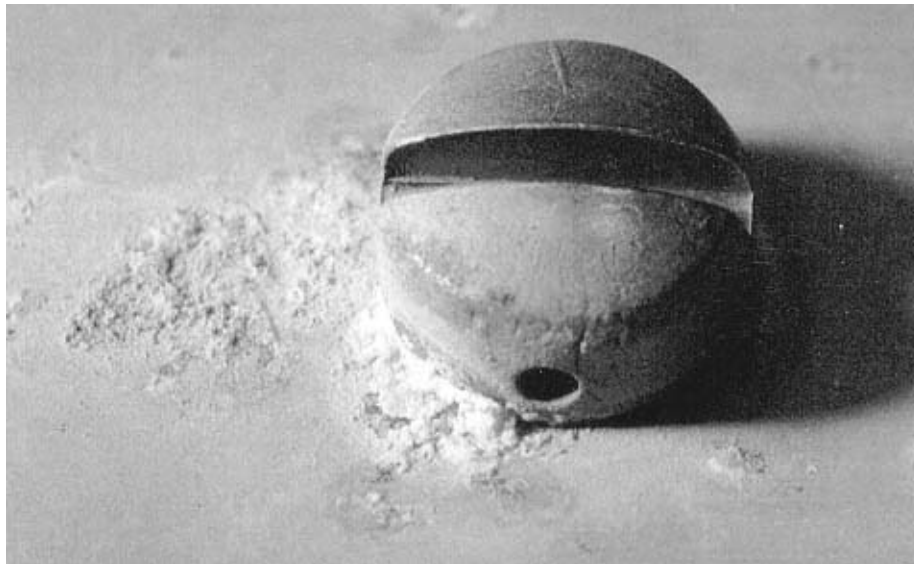
Figure 24   Galvanic Corrosion between a Stainless Steel Screw and Aluminum[2]

In general, corrosion is the result of an electrochemical reaction that occurs between an anode and a cathode. In the case of uniform corrosion, the metal being corroded acts as both the anode and the cathode in the reaction, where localized areas on the surface of the metal have slightly different electrical potentials. However, galvanic corrosion occurs between two dissimilar metals. The metal with a lower potential relative to the other metal acts as the anode, while the metal with

a higher potential acts as the cathode. The corrosion reaction/corrosion current (flow of electrical current) is driven by an electrical potential gradient. Some typical electrical potentials for some common metallic elements are shown in Table 18. (Note – these potentials were taken in standard conditions, but actual potentials vary in metals and alloys, especially under various environmental conditions.)

Table 18   Electromotive Series of Metals[9]

Metal	Ion Formed	Reactivity	Potential
Sodium	Na^+		-2.714
Magnesium	Mg^{++}		-2.363
Beryllium	Be^{++}		-1.847
Aluminum	Al^{+++}		-1.663
Titanium	Ti^{++}		-1.628
Manganese	Mn^{++}		-1.180
Zinc	Zn^{++}	Less Noble – Anodic	-0.763
Chromium	Cr^{++}		-0.744
Iron (Ferrous)	Fe^{++}		-0.440
Cadmium	Cd^{++}		-0.403
Cobalt	Co^{++}		-0.277
Nickel	Ni^{++}		-0.250
Tin	Sn^{++}		-0.136
Lead	Pb^{++}		-0.126
Iron (Ferric)	Fe^{+++}		~ -0.4
Hydrogen	H^+	Neutral	0.000
Antimony	Sb^{+++}		+0.152
Copper (Cupric)	Cu^{++}		+0.342
Copper (Cuprous)	Cu^+		+0.521
Mercury	Hg^{++}	More Noble – Cathodic	+0.788
Silver	Ag^+		+0.799
Palladium	Pd^{++}		+0.987
Platinum	Pt^{++++}		~ +1.2
Gold (Auric)	Au^{+++}		+1.498
Gold (Aurous)	Au^{++}		+1.691

4.2.1   Factors Influencing Galvanic Corrosion

There are a number of driving forces that influence the occurrence of galvanic corrosion and the rate at which it occurs. Among these influencing factors are the difference in the electrical potentials of the coupled metals, the relative area, and the system geometry. Other driving forces that factor into promoting or preventing galvanic corrosion include the polarization (the shift in electrode potential during electrolysis) of the metals, the electrical resistance and electrical current of the system, the type, pH, and concentration of the electrolyte, and the degree of aeration or motion of the electrolyte.[96]

4.2.1.1   Potential Difference

The main driving force for galvanic corrosion is the electrical potential difference between the two dissimilar metals; thus, typically the bigger the difference, the more rapid the rate of

galvanic corrosion. Galvanic corrosion occurs mainly at the contact area of the two metals and dissipates with distance from the junction. A fundamental expression that shows the electrical potential of a galvanic system is given in Equation 5.

$$E_c - E_a = I(R_e + R_m) \qquad \text{Equation 5}$$

where

E_c – electrical potential of the cathode $\qquad$ E_a – electrical potential of the anode

I – electrical current $\qquad\qquad\qquad\qquad$ R_m – resistance of the electrodes (external circuit)

R_e – resistance of the electrolyte solution path in the galvanic circuit (internal circuit)

There are numerous resources from which the standard electrode potentials of specific metals and alloys can be obtained. The rate of galvanic corrosion in specific environments, however, should not be determined based on the standard electrode potentials of metals. These standard potentials are determined as the potential of a metal in equilibrium with a specific concentration of the electrolyte.[96] Furthermore, a galvanic system is dynamic and the reactions are dependent on a number of other factors, including electrolyte concentration, temperature, and pH, as well as oxygen content and fluid motion.

It is not always necessary, however, to have two distinct metals in order to create a galvanic couple. There are instances where galvanic corrosion occurs within the same metal. This can happen when the metal has both an active and passive state, for example, one part is covered with an oxide film and hence passivated, while another part of the metal is exposed to the atmosphere. This condition would create a potential difference causing the unpassivated area of the metal to galvanically corrode.

4.2.1.2 Relative Area

The size of the metal components in the galvanic system also influences the rate and degree of corrosion. For example, a system with a relatively large cathode (less reactive metal) and a relatively small anode (more reactive metal) will corrode via galvanic corrosion to a greater extent than will a system with electrodes of equal size. Furthermore, a system with a relatively large anode compared to a small cathode will not typically exhibit galvanic corrosion on the anode to a significant extent. In general, corrosion of the anode is proportional to the relative area of the cathode. That is, the induced electrical current increases proportionally with an increase in cathodic area relative to the area of the anode. The opposite is generally true as well: current decreases proportionally with a decrease in relative cathodic area.

4.2.1.3 Geometry

Component geometry is another factor affecting the flow of current, which consequently influences the rate of galvanic corrosion. Current does not easily travel around corners, for instance.

4.2.1.4 Electrolyte and Environment

The rate of galvanic corrosion is partially dependent on the concentration, oxygen content and motion of the electrolyte, as well as the temperature of the environment. For instance, higher temperatures typically cause an increase in the rate of galvanic corrosion, while higher concentrations of the electrolyte will result in a decrease in the corrosion rate.96 The pH of the

electrolyte solution may also affect the occurrence of galvanic corrosion in a dissimilar metal system. For example, a metal that is the cathode in a neutral or basic electrolyte may become the anode if the electrolyte becomes acidic.96 A higher oxygen content in the electrolyte also typically results in an increase in the rate of galvanic corrosion. Electrolyte motion can also increase the rate of corrosion, since it may remove some of the oxidized metal from the anode surface, allowing for further oxidation of the metal.

4.2.2   Material Selection

In most cases, galvanic corrosion can be easily avoided if proper attention is given to the selection of materials during design of a system. It is often beneficial for performance and operational reasons for a system to utilize more than one type of metal, but this may introduce a potential galvanic corrosion problem. Therefore, sufficient consideration should be given to material selection with regard to the electrical potential differences of the metals.

4.2.2.1   Galvanic Series

The potential difference of two metals is qualitatively determined by their relative placement on the Galvanic Series, shown in Table 19. Some metals are listed more than once. This is either because they exhibit different galvanic properties when given different heat treatments, or because they can be in two different states. The metal is in an active state when the metal surface has direct interaction with the environment, and the metal is in a passive state when a noble film has formed on the surface.

This table can be helpful in estimating the likelihood of corrosion of a specified bimetallic system by gauging the distance between the two metals on the galvanic series. To state it simply, avoid using metals that are far apart on the galvanic series. The chart is not useful, however, in predicting the degree or rate of corrosion, since there are several other factors that influence the magnitude of corrosion in a given bimetallic system.

The metal that is higher on the Galvanic Series chart is less reactive and thus acts as the cathode, while the metal appearing lower in the series is more reactive and acts as the anode in the electrochemical cell. For example, if copper was to be electrically coupled with tin and immersed in seawater, then copper would be the anode and would corrode more readily than tin, which would act as the cathode. In environments other than seawater, the metal with the least resistance to corrosion in the surroundings acts as the anode and is then more readily corroded than the other, more noble metal.

4.2.2.2   Other Material Selection Charts

There have been a number of charts and tables created in order to aid in the material selection process and eliminate the potential for galvanic corrosion. Table 20 lists specific metal and alloy compatibilities with other specific metals and alloys in seawater with respect to galvanic corrosion. This table shows whether a certain combination of metals or alloys is compatible, unfavorable or uncertain. Note that the stainless steels listed in the table are all in the same state (active or passive). Table 21, on the other hand, lists metal and alloy compatibilities with respect to galvanic corrosion in environments other than seawater, such as marine and industrial atmospheres.

Table 19   Galvanic Series in Seawater[2, 10, 96]

Noble (least active)

Platinum	Silicon bronze	Cast iron
Graphite	Stainless Steel, 17-7 PH (passive)	Mild steel
Gold	Stainless Steel, Type 309 (passive)	Aluminum Alloy 5052-H16
Titanium	Stainless Steel, Type 321 (active)	Aluminum Alloy 2024-T4
Silver	Carpenter 20 (active)	Aluminum Alloy 2014-0
AM350 (passive)	Stainless Steel, Type 201 (active)	Indium
Titanium 75A	Monel 400	Aluminum Alloy 6061-0
Titanium 13V-11Cr-3 Al (solution treated and aged)	Stainless Steel, Type 202 (active)	Aluminum Alloy 1160-H14
Titanium 8Mn	Copper	Aluminum Alloy 7075-T6
Titanium 6Al-4V (annealed)	Red brass	Aluminum Alloy A360 (die cast)
Titanium 6Al-4V (solution treated and aged)	Molybdenum	Aluminum Alloy 6061-T6
Titanium 13V-11Cr-3Al (annealed)	Stainless Steel, Type 347L (active)	Aluminum Alloy 3003-H25
Titanium 5Al-2.5Sn	Aluminum bronze	Aluminum Alloy 1100-0
Chlorimet 3	Admiralty brass	Aluminum Alloy 5052-H32
Hastelloy C	Yellow brass	Aluminum Alloy 5456-0, H353
Stainless Steel, Type 286 (passive)	Chlorimet 2	Aluminum Alloy 5052-H12
AM355 (passive)	Hastelloy B	Aluminum Alloy 5052-0
Carpenter 20 (passive)	76Ni-16Cr-7Fe alloy (active)	Aluminum Alloy 218 (die cast)
Stainless Steel, Type 202 (passive)	Nickel (active)	Uranium
AM355 (active)	Naval brass	Cadmium
Stainless Steel, Type 316 (passive)	Manganese bronze	Aluminum Alloy 7079-T6
Stainless Steel, Type 286 (active)	Muntz metal	Aluminum Alloy 1160-H14
Stainless Steel, Type 201 (passive)	Tungsten	Aluminum Alloy 2014-T3
Stainless Steel, Type 321 (passive)	Stainless Steel 17-7 PH (active)	Alclad
Stainless Steel, Type 301 (passive)	Stainless Steel, Type 430 (passive)	Aluminum 6053
Stainless Steel, Type 304 (passive)	Stainless Steel, Type 301 (active)	Galvanized steel
Stainless Steel, Type 410 (passive)	Stainless Steel, Type 310 (active)	Beryllium (hot pressed)
7Ni-33Cu alloy	AM350 (active)	Zinc
75Ni-16Cr-7Fe alloy (passive)	Tantalum	Magnesium alloys
Nickel (passive)	Tin	Magnesium
Silver solder	Lead	
M-Bronze	Stainless Steel, Type 316 (active)	**Anodic (most active)**
G-Bronze	Stainless Steel, Type 304 (active)	
70-30 cupro-nickel	Stainless Steel, Type 410 (active)	

Table 20   GalvanicCorrosion Compatibilities of Metals and Alloys in Seawater[11]

S - Small Metal A to Metal B Area Ratio   ●   Unfavorable - Galvanic Acceleration Expected
E - Equal Area Ratio   x   Uncertain - Variable Direction and/or Magnitude of Galvanic Effect
L - Large Metal A to Metal B Area Ratio   o   Compatible - No Galvanic Acceleration Expected

Column abbreviations (Metal B →):
1 = Magnesium Alloys; 2 = Zinc; 3 = Aluminum Alloys; 4 = Cadmium; 5 = Mild Steel, Wrought Iron; 6 = Cast Iron; 7 = Low Alloy High Strength Steel; 8 = Brasses, Mn Bronze; 9 = Copper, Si Bronze; 10 = Lead-Tin Solder; 11 = Tin Bronze (G & M); 12 = 90/10 Copper-Nickel; 13 = 70/30 Copper-Nickel; 14 = Nickel-Aluminum Bronze; 15 = Silver Braze Alloys; 16 = Types 302, 304, 321 & 347 Stainless Steel; 17 = Alloys 400, K-500; 18 = Types 316 & 317 Stainless Steel; 19 = Alloy 20, Alloy 825; 20 = Titanium, Alloys C, C-276, 625; 21 = Graphite, Graphitized Cast Iron

(■ = diagonal / self cell)

Metal A ↓	Ratio	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Magnesium Alloys	S	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	■	●	x	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Zinc	S	●	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	■	x	x	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	●	■	o	o	o	o	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●
Aluminum Alloys	S	●	o	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	x	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	●	●	■	x	x	x	x	●	●	●	●	●	●	●	●	x	●	x	x	x	●
Cadmium	S	x	o	x	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	x	●	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	●	●	●	■	o	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Mild Steel, Wrought Iron	S	●	o	x	o	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	●	●	●	■	o	x	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	●	●	●	●	■	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
Cast Iron	S	●	o	x	o	o	■	x	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	●	●	●	o	■	x	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	●	●	●	●	●	■	●	x	x	x	x	x	x	x	x	x	x	x	x	o	x
Low Alloy High Strength Steel	S	●	o	x	o	o	●	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	●	●	x	x	●	■	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	L	●	●	●	●	●	x	■	o	o	o	o	o	o	o	o	o	o	o	o	o	o
Brasses, Mn Bronze	S	●	●	●	●	o	x	o	■	●	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	●	●	●	●	●	●	■	x	x	x	x	x	x	x	●	●	x	x	x	●
	L	●	●	●	●	●	●	x	■	x	x	x	x	x	x	x	o	x	o	o	o	●
Copper, Si Bronze	S	●	●	●	●	o	x	o	x	■	●	●	●	●	●	●	●	●	●	●	●	●
	E	●	●	●	●	●	●	●	x	■	x	x	x	x	x	●	x	x	x	x	x	●
	L	●	●	●	●	●	●	●	●	■	x	x	x	x	x	●	x	o	●	o	o	●
Lead-Tin Solder	S	●	●	●	●	o	o	o	x	x	■	x	x	x	●	x	●	●	x	●	●	●
	E	●	●	●	●	●	●	●	x	x	■	x	o	o	o	o	o	●	x	x	o	●
	L	●	●	●	●	●	●	●	●	●	■	x	x	x	o	o	o	●	o	o	o	●
Tin Bronze (G & M)	S	●	●	●	●	o	x	o	x	x	x	■	x	x	x	●	x	x	x	x	x	●
	E	●	●	●	●	●	●	●	x	x	x	■	o	x	x	●	x	●	x	x	x	●
	L	●	●	●	●	●	●	●	●	●	●	■	x	o	x	●	o	x	o	x	o	●
90/10 Copper-Nickel	S	●	●	●	●	o	x	o	x	x	x	x	■	●	x	x	●	●	●	●	●	●
	E	●	●	●	●	●	●	●	x	x	o	o	■	o	o	x	●	x	x	x	x	●
	L	●	●	●	●	●	●	●	●	x	x	●	■	o	o	x	●	o	o	o	o	●
70/30 Copper-Nickel	S	●	●	●	●	o	x	o	x	x	x	o	o	■	o	x	●	x	x	x	●	●
	E	●	●	●	●	●	●	●	x	x	o	x	o	■	o	x	●	x	x	o	o	●
	L	●	●	●	●	●	●	●	●	x	x	●	●	■	o	o	●	o	o	o	o	●
Nickel-Aluminum Bronze	S	●	●	●	●	o	x	o	x	x	x	o	o	o	■	x	●	●	●	●	●	●
	E	●	●	●	●	●	●	●	x	x	o	o	o	o	■	x	●	x	x	x	x	●
	L	●	●	●	●	●	●	●	●	x	x	x	x	o	■	x	●	o	o	o	o	●
Silver Braze Alloys	S	●	●	●	●	o	x	o	x	x	x	x	x	x	x	■	●	x	x	x	x	●
	E	●	●	●	●	●	●	●	●	x	●	x	x	x	x	■	●	x	x	x	x	●
	L	●	●	●	●	●	●	●	●	●	●	●	x	x	x	■	x	x	x	x	x	●
Types 302, 304, 321 & 347 Stainless Steel	S	●	●	x	●	o	x	o	x	x	x	x	●	●	●	●	■	●	●	●	●	●
	E	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	■	●	●	●	●	●
	L																■			x		
Alloys 400, K-500	S	●	●	●	●	o	o	o	o	o	o	o	o	o	o	x	x	■	x	x	x	●
	E	●	●	●	●	●	●	●	x	o	x	x	x	x	x	●	●	■	x	x	x	●
	L	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	■	x	x	x	●
Types 316 & 317 Stainless Steel	S	●	●	x	●	o	x	o	x	x	x	x	●	●	●	●	●	●	■	x	x	●
	E	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	■	x	x	●
	L																		■	x	x	●
Alloy 20, Alloy 825	S	●	●	x	●	o	o	o	●	x	o	o	o	o	o	o	x	●	x	■	x	●
	E	●	●	●	●	●	●	●	x	x	x	o	x	o	x	x	●	x	x	■	x	●
	L	●	●	●	●	●	●	●	●	●	●	●	●	●	x	●	●	x	x	■	x	●
Titanium, Alloys C, C-276, 625	S	●	●	x	●	o	o	o	o	o	o	o	o	o	o	o	x	●	x	x	■	x
	E	●	●	●	●	x	x	x	x	x	x	x	o	x	o	x	●	x	x	x	■	x
	L	●	●	●	●	●	●	●	●	x	x	●	x	x	x	x	x	x	x	x	■	x
Graphite, Graphitized Cast Iron	S	●	●	●	●	x	●	●	●	●	●	●	●	●	●	●	●	●	●	●	x	■
	E	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	x	■
	L	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	x	■

Table 21   Galvanic Corrosion Compatibilities of Metals and Alloys in Marine and Industrial Environments[96]

M - Marine Atmosphere   ● Unfavorable - Galvanic Acceleration Expected or Uncertain
I - Industrial Atmosphere   o Compatible - No Galvanic Acceleration Expected

Material	Env	Zinc, Zinc Coating	Cadmium, Beryllium	Aluminum, Mg-Coated Aluminum, Zn-Coated Aluminum	Cu-Coated Aluminum	Steels-Carbon, Low Alloy	Lead	Tin, Tin-Lead, Indium	St. Steels - Martensitic, Ferritic	Chromium, Molybdenum, Tungsten	St. Steels-Aust., PH, Super Strength, Heat Resist	Brass-Lead Bronze	Brass-Low Copper, Bronze-Low Copper	Brass-High Copper, Bronze-High Copper	Copper-High Nickel, Monel	Nickel, Cobalt	Titanium	Silver	Palladium, Rhodium, Gold, Platinum	Graphite
Magnesium	M	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	I	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Zinc, Zinc Coating	M		o	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	I		o	o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Cadmium, Beryllium	M			o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	I			o	o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Aluminum, Mg-Coated Aluminum, Zn-Coated Aluminum	M				o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	I				o	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Cu-Coated Aluminum	M					●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
	I					●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Steels-Carbon, Low Alloy	M						●	●	●	●	●	●	●	●	●	o	●	●	●	●
	I						o	●	●	●	●	●	●	●	●	o	●	●	●	●
Lead	M							o	o	o	o	o	●	●	●	●	●	o	●	●
	I							o	o	o	o	o	●	o	o	o	o	o	o	o
Tin, Tin-Lead, Indium	M								●	●	●	o	o	o	o	o	o	o	●	●
	I								●	o	o	o	o	o	o	o	o	o	●	●
St. Steels - Martensitic, Ferritic	M									●	●	●	●	●	●	●	●	●	●	●
	I									o	●	●	o	●	●	●	●	●	●	●
Chromium, Molybdenum, Tungsten	M										o	o	●	●	o	o	o	o	o	o
	I										o	o	o	●	o	o	o	o	o	o
St. Steels-Aust., PH, Super Strength, Heat Resistant	M											●	●	●	o	o	o	o	o	o
	I											●	●	●	o	o	o	o	o	o
Brass-Lead Bronze	M												o	o	●	o	●	o	o	o
	I												o	o	o	o	o	o	o	o
Brass-Low Copper, Bronze-Low Copper	M													o	o	●	o	●	●	●
	I													o	o	o	o	o	o	o
Brass-High Copper, Bronze-High Copper	M														●	o	●	o	●	●
	I														o	o	o	o	o	o
Copper-High Nickel, Monel	M															o	o	o	o	o
	I															o	o	o	o	o
Nickel, Cobalt	M																o	o	o	o
	I																o	o	o	o
Titanium	M																	o	o	o
	I																	o	o	o
Silver	M																		o	o
	I																		o	o
Palladium, Rhodium, Gold, Platinum	M																			o
	I																			o

Note – Joined metals presented in this table are of equal area.
PH – Precipitation Hardening is a specific type of heat treatment/aging

4.2.3   Managing Galvanic Corrosion

If proper design, material selection, implementation, and maintenance steps are followed, it is relatively simple to avoid the occurrence of galvanic corrosion in a new system. MIL-STD-889 (active) is a DOD standard on dissimilar metals. The purpose of this standard is to define and classify dissimilar metals and establish requirements for protecting coupled dissimilar metals in all military equipment parts, components and assemblies.[96] To further aid in properly avoiding this form of corrosion, Table 22 provides a brief list of guidelines to minimize galvanic corrosion. Some of these are explained in more detail in the sections to follow.

Table 22   Guidelines for Minimizing Galvanic Corrosion[11]

- Use one material to fabricate electrically isolated systems or components where practical.
- If mixed metal systems are used, select combinations of metals as close together as possible in the galvanic series, or select metals that are galvanically compatible.
- Avoid the unfavorable area effect of a small anode and large cathode. Small parts or critical components such as fasteners should be the more noble metal.
- Insulate dissimilar metals wherever practical [for example, by using a gasket]. It is important to insulate completely if possible.
- Apply coatings with caution. Keep the coatings in good repair, particularly the one on the anodic member.
- Add inhibitors, if possible, to decrease the aggressiveness of the environment.
- Avoid threaded joints for materials far apart in the series.
- Design for the use of readily replaceable anodic parts or make them thicker for longer life.
- Install a third metal that is anodic to both metals in the galvanic contact.

4.2.3.1   Area Effects

Taking into account the relative areas of galvanically coupled metallic systems can minimize galvanic corrosion. The size of the cathodic metal in the bimetallic system should not be significantly larger than the size of the anodic metal, since this would cause a greater degree of corrosion of the anodic member. Instead, the anodic metal should have an equal or larger area. For example, the more noble metal should be used for rivets, bolts and other fasteners, thus making the area of the anode much greater than that of the cathodic component.

4.2.3.2   Cathodic Protection

Galvanic corrosion can be intentionally induced in order to protect a more important metallic component. This method of protection involves using a highly active metal, one that is lower on the galvanic series, to be sacrificially corroded. This sacrificial anode protects the more important, cathodic metal from corrosion. Magnesium and zinc are commonly used as sacrificial anodes. Sacrificial anodes are often replaced in-service as they are consumed through galvanic corrosion, as intended.

4.2.3.3   Insulate Dissimilar Metals

Electrically resistive, non-metallic materials can be used to insulate two dissimilar metals. This in effect, breaks the electrical connection or at least increases the electrical resistivity resulting in a reduction, if not elimination, of the potential for galvanic corrosion.

4.2.3.4   Coatings

Metallic coatings are commonly used to protect bimetallic systems against galvanic corrosion. These coatings can provide protection by acting as barriers to corrosion or by readily accepting corrosion, thereby saving the important metal component from being corroded. For example, zinc is often used as a coating for steel, and since it is not very corrosion resistant, it will corrode preferentially to protect the steel. Thus, the zinc coating acts as a sacrificial anode.

Noble metal coatings are typically used as barrier coatings, since they are relatively unreactive. These coatings can isolate the important metal from the surrounding environment; however, pores, defects, or damaged areas in these barrier coatings are areas still susceptible to being galvanically corroded. Furthermore, the areas under these discontinuities (also known as holidays) in the coating system are likely to be targeted for severe localized corrosion. In addition, if the anodic metal in the galvanically coupled system is coated with a barrier coating without coating the cathodic member as well, it can have severe negative effects due to the reduced anodic area. Moreover, if the anode is coated, while the cathode is not, the former cathode may become anodic to the former anode.

4.2.3.5   Crevices

Threaded joints with dissimilar metals that are far apart on the galvanic series should be avoided. It is recommended that crevices be sealed either by welding or brazing to protect against galvanic corrosion.

4.3   Crevice Corrosion

Crevice corrosion occurs as a result of water or other liquid entrapment in localized areas dependent upon component/system design. These designs include primarily sharp angles, fasteners, joints, washers and gaskets. Crevice corrosion can also occur under debris build up on surfaces, sometimes referred to as "poultice corrosion." Poultice corrosion can be quite severe, due to an increasing acidity in the crevice area.

4.3.1   Crevice Corrosion Mechanism

The combination of low oxygen content in the crevice area compared to the surroundings, sets up an anodic imbalance creating a highly corrosive microenvironment, as depicted in Figure 25. Crevice corrosion is of particular concern in aircraft lap joints. In severe cases, the build up of corrosion products in the lap joint can cause separation of the two metals, known as pillowing.

Local acidification of electrolyte by the reactions:

$$Fe^{2+} + 2Cl^- \rightarrow FeCl_2 \text{ (unstable)}$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$$
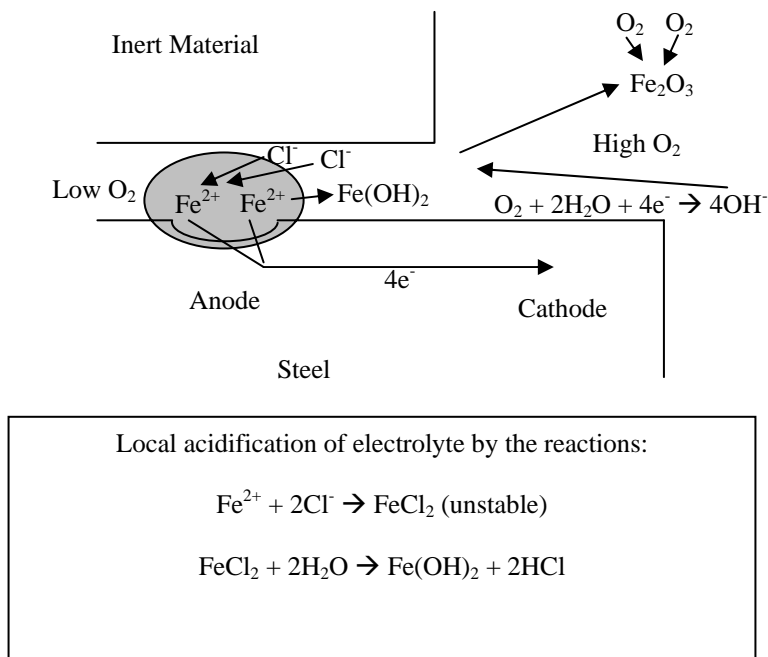
Figure 25   Crevice Corrosion Process in Steel[6]

4.3.2   Crevice Geometry

The crevice gap, depth, and the surface ratios of materials can all affect the degree of crevice corrosion. Tighter gaps have been known to increase the rate of crevice corrosion of stainless steels in chloride environments. This has been attributed to the reduced volume of electrolyte that becomes acidified resulting in a higher rate of attack. The larger crevice depth and greater surface area of metals will generally increase the rate of crevice corrosion.

4.3.3   Metals Susceptible to Crevice Corrosion

In general, materials that are passive have a greater susceptibility to crevice corrosion. These include aluminum alloys and particularly stainless steels. Titanium alloys normally have good resistance to crevice corrosion. However, they may become susceptible in elevated temperature, acidic environments containing chlorides.   In seawater environments, copper alloys can experience crevice corrosion that occurs on the outside of the crevice.

4.3.4   Managing Crevice Corrosion

New components and systems should be designed to minimize areas where crevice corrosion may occur. Welded joints are preferable to fastened joints. Where crevices are unavoidable, metals with a greater resistance to crevice corrosion in the intended environment should be selected. Avoid the use of hydrophilic materials in fastening systems and gaskets. Crevice areas should be sealed to prevent the ingress of water. Also, a regular cleaning schedule should be implemented to remove any debris build up. Figure 26 illustrates several methods that may be implemented to decrease crevice corrosion.
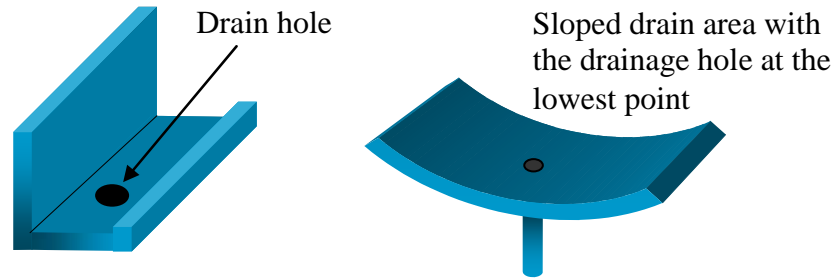
(a) Avoid buildup of corrosive debris
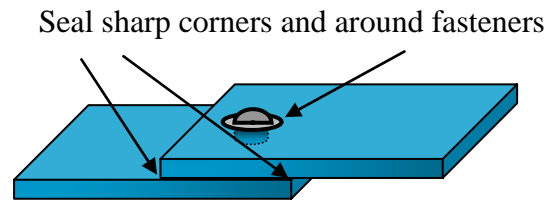
(b) Prevent the ingress of liquids

Figure 26   Methods to Mitigate Crevice Corrosion

4.4   Pitting Corrosion

Pitting corrosion, also simply known as pitting, is an extremely localized form of corrosion that occurs when a corrosive medium attacks a metal at specific points causing small holes or pits to form.   This usually happens when a protective coating or oxide film is perforated, due to mechanical damage or chemical degradation. Pitting can be one of the most dangerous forms of corrosion because it is difficult to anticipate and prevent, relatively difficult to detect, occurs very rapidly, and penetrates a metal without causing it to lose a significant amount of weight. Failure of a metal due to the effects of pitting corrosion can thus occur very suddenly. Pitting can have side effects too, for example, cracks may initiate at the edge of a pit due to an increase in the local stress. In addition, pits can coalesce underneath the surface, which can weaken the material considerably. Figure 27 shows the result of pitting of an aluminum railing that was located near an ocean.

Figure 27   Pitting Corrosion of an Aluminum Railing near the Atlantic Ocean[2]

4.4.1   Pitting Mechanism

Pitting often begins at a specific area of a passivated metal where there is a break in the passivation layer, which then acts as the anodic area, while the rest of the metal acts as the cathodic area. With a potential difference between the anode and cathode, extremely localized corrosion initiates, and since the surrounding area is passivated, the corrosion remains localized and causes pits to form in the metal. Moreover, since the anodic area is significantly smaller than the cathodic area, corrosion continues at a rapid pace.

A further danger of pitting is that corrosion in pits becomes self-sustaining by an autocatalytic process. Such a process involves the progression of pit growth by the dissolution of the metal near the bottom of the pit. It is thought that the environment is very acidic near the bottom of the pit, thus propagating the dissolution of the metal. The dissolution reaction, where electrons associated with a metal-metal bond are dispelled and a metal ion breaks away from the bulk material, works in conjunction with a cathodic reaction near the surface adjacent to the pit. The cathodic reaction supplies excess electrons to facilitate a reduction reaction by forming hydroxide ions from water molecules and diatomic oxygen. To maintain neutrality, anions (negative ions) from the electrolyte migrate into the pit where there is an excess of positive charge, and associate with the metal ions. Subsequently, this species is dissociated in water to form a metal hydroxide and an acid, which results in a reduction in the pH near the bottom of the pit. This means that there is an excess of positively charged hydrogen ions and anions, which stimulate and propagate further dissolution of the metal near the bottom of the pit. These reactions are shown in Equation 6, Equation 7, and Equation 8.

$$M \rightarrow M^{n+} + ne^-$$ 　　　　　Equation 6

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$ 　　　　　Equation 7

$$M^+I^- + H_2O \rightarrow MOH + H^+I^-$$ 　　　　　Equation 8
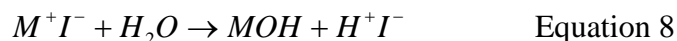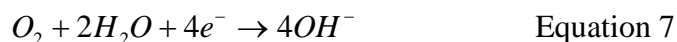
where

M – metal

M^+ – metal ion

e^- – electron

I^- – anion (i.e. Cl^-)

Pitting corrosion is also very difficult to measure and predict, as there are usually numerous pits of varying depths and diameters, which do not form consistently under specified conditions. The holes that form from corrosive attack, however, tend to be greater in depth than in diameter. These pits typically form on the top-surface of a metal and proceed to deepen in the same direction as gravity. Thus, they do not usually form on surface planes that are parallel to the direction of gravity, but rather on those that are perpendicular to gravity. Moreover, pits do not tend to proceed away from the direction of gravity. Basically, they do not form on the bottom surface of a metal and proceed away from the direction of gravity. Initiation of the holes is a gradual and fairly long process, but once they are formed, the rate of growth of the pit increases significantly. Pitting usually occurs in static or low velocity fluid systems, since pitting corrosion will tend to decrease as fluid velocity increases. Pitting is often difficult to measure since the metal usually experiences minimal weight loss during the corrosion process. Also, pits can be filled in with corrosion products.

4.4.2   Metals Susceptible to Pitting Corrosion

Stainless steels tend to be the most susceptible to pitting corrosion among metals and alloys. For example, stainless steels tend to form deep pits in seawater, and environments containing higher concentrations of chlorine or bromine solutions. Polishing the surface of stainless steels can increase the resistance to pitting corrosion compared to etching or grinding the surface. Alloying can have a significant impact on the pitting resistance of stainless steels. The effects of some of the alloying elements of stainless steels on the corresponding resistance to pitting are provided in Table 23.

Table 23   Effects of Alloying Elements on Pitting Resistance of Stainless Steel Alloys[12]

Element	Effect on Pitting Resistance
Chromium	Increases
Nickel	Increases
Molybdenum	Increases
Silicon	Decreases; increases when present with molybdenum
Titanium and Niobium	Decreases resistance in $FeCl_3$; other mediums no effect
Sulfur and Selenium	Decreases
Carbon	Decreases, especially in sensitized condition
Nitrogen	Increases

Conventional steel has a greater resistance to pitting corrosion than stainless steels, but is still susceptible, especially when unprotected. Aluminum in an environment containing chlorides and aluminum brass in contaminated or polluted water are usually susceptible to pitting. Titanium is strongly resistant to pitting corrosion. The relative pitting resistance of some metals is shown in Figure 28.

Increasing
Pitting
Resistance

Titanium
Hastelloy C or Chlorimet 3
Hastelloy F, Nionel or Durimet 20
Type 316 SS
Type 304 SS
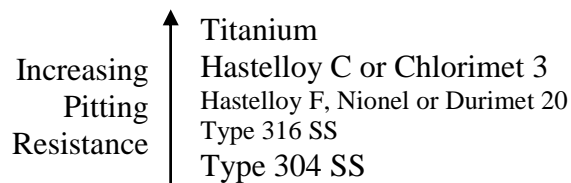
Figure 28   Relative Pitting Resistance of Some Metals

4.4.3   Managing Pitting Corrosion

Proper material selection is very effective in preventing the occurrence of pitting corrosion. Field testing, though, is often necessary to determine whether the chosen material is suitable for the proposed environment. Another option for protecting against pitting is to mitigate aggressive environments and environmental components (e.g. chloride ions, low pH, etc.). Inhibitors may sometimes stop pitting corrosion completely. Further efforts during design of the system can aid in preventing pitting corrosion, for example, by eliminating stagnant solutions or by the inclusion of cathodic protection.

4.5   Intergranular Corrosion

Intergranular corrosion attacks the interior of metals along grain boundaries. It is associated with impurities which tend to deposit at grain boundaries and/or a difference in phase precipitated at grain boundaries. Heating of some metals can cause a "sensitization" or an increase in the level of inhomogeniety at grain boundaries. Therefore, some heat treatments and weldments can result in a propensity for intergranular corrosion. Susceptible materials may also become sensitized if used in operation at a high enough temperature environment to cause such changes in internal crystallographic structure.

4.5.1   Metals Susceptible to Intergranular Corrosion

Intergranular corrosion can occur in many alloys. The most predominant susceptibilities have been observed in stainless steels and some aluminum and nickel-based alloys. Stainless steels, especially ferritic stainless steels, have been found to become sensitized, particularly after welding. Welding causes the precipitation chromium carbide phases at grain boundaries in the heat affected zone (HAZ). This in turn results in intergranular corrosion within the HAZ of the stainless steels. Section 6.1.2.4 provides more information of the susceptibility of stainless steels to intergranular corrosion. Aluminum alloys also suffer intergranular attack as a result of precipitates at grain boundaries that are more active. Alloys that fall into this type of corrosion include 5083, 7030, 2024, and 7075, refer to Section 6.2.2.4. Exfoliation corrosion is considered a type of intergranular corrosion in materials that have been mechanically worked to produce elongated grains in one direction. This form of corrosion has been experienced in certain aluminum alloys and is covered in Section 4.9.5. High nickel alloys can be susceptible by precipitation of intermetallic phases at grain boundaries. The intergranular corrosion process is however more complicated in nickel-alloys than in stainless steels or aluminum alloys. Nickel-alloy susceptibilities are further covered in Section 6.4.2.4.

4.5.2   Managing Intergranular Corrosion

Methods to limit intergranular corrosion include:

- Keep impurity levels to a minimum
- Proper selection of heat treatments to reduce precipitation at grain boundaries.
- Specifically for stainless steels, reduce the carbon content, and add stabilizing elements (Ti, Nb, Ta) which preferentially form more stable carbides than chromium carbide.

4.6   Selective Leaching (Dealloying Corrosion)

Dealloying, also called selective leaching, is a rare form of corrosion where one element is targeted and consequently extracted from a metal alloy, leaving behind an altered structure. The most common form of selective leaching is dezincification, where zinc is extracted from brass alloys or other alloys containing significant zinc content. Left behind are structures that have experienced little or no dimensional change, but whose parent material is weakened, porous and brittle. Dealloying is a dangerous form of corrosion because it reduces a strong, ductile metal to one that is weak, brittle and subsequently susceptible to failure. Since there is little change in the metal's dimensions dealloying may go undetected, and failure can occur suddenly. Moreover, the porous structure is open to the penetration of liquids and gases deep into the metal, which can result in further degradation. Selective leaching often occurs in acidic environments.

4.6.1   Dezincification

There are essentially two forms of dezincification: uniform and localized.   Uniform dezincification occurs when zinc is leached from a broad area of the brass surface, whereas, the localized form, also known as plug-type dezincification, penetrates deeply into the brass. In the localized form, the metal in the surrounding area is not significantly corroded by dezincification.

The widely accepted mechanism of dezincification involves the dissolution of brass where the zinc remains suspended in the corrosive solution while the copper is plated back on to the brass. Although dezincification can occur in the absence of oxygen, its presence accelerates the corrosion rate. Copper-zinc alloys with greater than 15% zinc are susceptible to dezincification. Figure 29 shows a photograph of corrosion by dezincification.

Figure 29   Dezincification of Brass Containing a High Zinc Content[13]

4.6.2   Susceptible Metals

Although brass with a relatively high zinc content is the most common alloy to experience the selective leaching form of corrosion, other metals and alloys, as shown in Table 24, are susceptible to this form of corrosion.

4.6.3   Managing Selective Leaching

Reducing the aggressive nature of the atmosphere by removing oxygen and avoiding stagnant solutions/debris buildup can prevent dezincification. Cathodic protection can also be used for prevention. However, the best alternative, economically, may be to use a more resistant material such as red brass, which only contains 15% Zn.   Adding tin to brass also provides an improvement in the resistance to dezincification. Additionally, inhibiting elements, such as arsenic, antimony and phosphorous can be added in small amounts to the metal to provide further improvement. Avoiding the use of a copper metal containing a significant amount of zinc altogether may be necessary in systems exposed to severe dezincification environments.

Table 24   Combinations of Alloys and Environments Subject to Dealloying and Elements Preferentially Removed

Alloy	Environment	Element Removed
Brasses	Many waters, especially under stagnant conditions	Zinc (dezincification)
Gray Iron	Soils, many waters	Iron (graphitic corrosion)
Aluminum Bronzes	Hydrofluoric acid, acids containing chloride ions	Aluminum (dealuminification)
Silicon Bronzes	High-temperature steam and acidic species	Silicon (desiliconification)
Tin Bronzes	Hot brine or steam	Tin (destannification)
Copper Nickels	High heat flux and low water velocity (in refinery condenser tubes)	Nickel (denickelification)
Copper-Gold (single crystals)	Ferric chloride	Copper
Monels	Hydrofluoric and other acids	Copper in some acids, and nickel in others
Gold Alloys with Cu or Ag	Sulfide solutions, human saliva	Copper, silver
High-Nickel Alloys	Molten salts	Chromium, iron, molybdenum and tungsten
Medium- and High-Carbon Steels	Oxidizing atmospheres, hydrogen at high temperatures	Carbon (decarburization)
Iron-Chromium Alloys	High-temperature oxidizing atmospheres	Chromium, which forms a protective film
Nickel-Molybdenum Alloys	Oxygen at high temperature	Molybdenum

4.7   Erosion Corrosion

Erosion corrosion is a form of attack resulting from the interaction of an electrolytic solution in motion relative to a metal surface. It has typically been thought of as involving small solid particles dispersed within a liquid stream. The fluid motion causes wear and abrasion, increasing rates of corrosion over uniform (non-motion) corrosion under the same conditions. Erosion corrosion is evident in pipelines, cooling systems, valves, boiler systems, propellers, impellers, as well as numerous other components. Specialized types of erosion corrosion occur as a result of impingement and cavitation. Impingement refers to a directional change of the solution whereby a greater force is exhibited on a surface such as the outside curve of an elbow joint. Cavitation is the phenomenon of collapsing vapor bubbles which can cause surface damage if they repeatedly hit one particular location on a metal.

4.7.1   Factors Affecting Erosion Corrosion

All the factors that influence the resistance of material to erosion corrosion and their exact relationship are difficult to define. One property that factors in is hardness. In general harder materials resist erosion corrosion better, but there are some exceptions. Surface smoothness, fluid velocity, fluid density, angle of impact, and the general corrosion resistance of the material to the environment are other properties that factor in. Equation 9 predicts the erosion rate of metals using some of these factors. However, this prediction is only for erosion and does not

include the added effects of corrosion. Erosion in a corrosive environment would be expected to occur at a higher rate.

$$\frac{\text{Erosion loss}}{\text{Quantity of impacting erodent}} = CF(\varphi)\frac{\rho v^2}{HV}$$

Equation 9

where,

C is a system constant

φ is the angle of impact

ρ is the density of the erodent

v is the erodent velocity

HV is the hardness of the metal

4.7.2   Managing Erosion Corrosion

There are some design techniques that can be used to limit erosion corrosion as listed below with a couple methods depicted in Figure 30.

Avoid turbulent flow.

Add deflector plates where flow impinges on a wall.

Add plates to protect welded areas from the fluid stream.

Put piping of concentrate additions vertically into the center of a vessel.

(a) protect weldments

(a) protect impingement areas
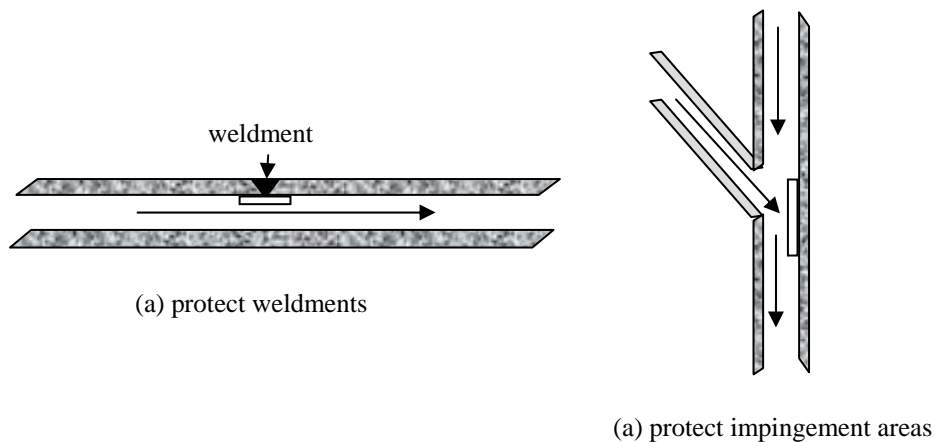
Figure 30   Techniques to Combat Erosion Corrosion

4.8   Stress-Corrosion Cracking

Stress corrosion is an environmentally induced cracking phenomenon that sometimes occurs when a metal is subjected to a tensile stress and a corrosive environment simultaneously. This is not to be confused with similar phenomena such as hydrogen embrittlement, in which the metal is embrittled by hydrogen, often resulting in the formation of cracks. Moreover, SCC is not

defined as the cause of cracking that occurs when the surface of the metal is corroded resulting in the creation of a nucleating point for a crack. Rather, it is a synergistic effort of a corrosive agent and a modest, static stress. Another form of corrosion similar to SCC, although with a subtle difference, is corrosion fatigue, and is discussed in Section 4.9.1. The key difference is that SCC occurs with a static stress, while corrosion fatigue requires a dynamic or cyclic stress.

Stress corrosion cracking (SCC) is a process that takes place within the material, where the cracks propagate through the internal structure, usually leaving the surface unharmed. Furthermore, there are two main forms of SCC, intergranular and transgranular. For the intergranular form, the cracking progresses mostly along grain boundaries, whereas, in transgranular SCC, the cracking does not strictly adhere to the grain boundaries, instead it can penetrate grains. Most cracks tend to propagate in a direction that is perpendicular to the direction of applied stress. Aside from an applied mechanical stress, a residual, thermal, or welding stress along with the appropriate corrosive agent may also be sufficient to promote SCC. Pitting corrosion, especially in notch-sensitive metals, has been found to be one cause for the initiation of SCC.

SCC is a dangerous form of corrosion because it can be difficult to detect, and it can occur at stress levels which fall within the range that the metal is designed to handle. Furthermore, the mechanism of SCC is not well understood. There are a number of proposed mechanisms that attempt to explain the phenomenon of SCC, but none have done so with complete success. Figure 31 shows pictures of the two types of stress corrosion cracking.

(a)   (b)
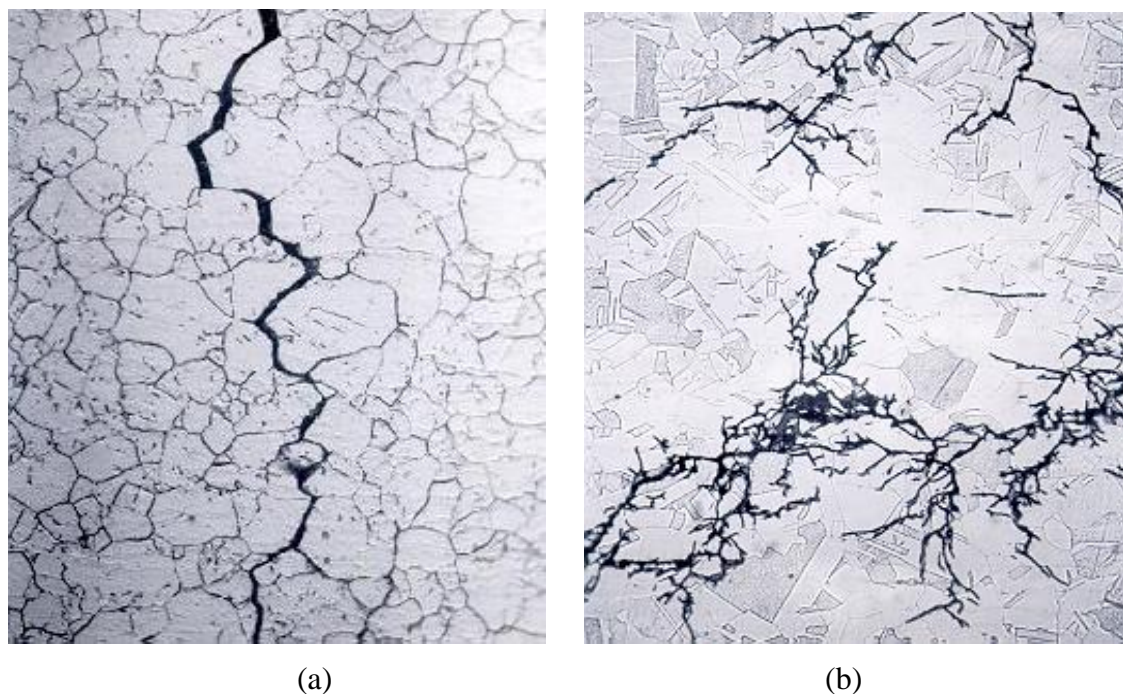
Figure 31   Pictures of Stress Corrosion Cracking, (a) Intergranular, (b) Transgranular[14]

4.8.1   Environmental Influence on SCC

Stress corrosion cracking is dependent on the environment based on a number of factors including temperature, solution, metallic structure and composition, and stress.[12] However, not all environments are equally potent to all metals; that is, specific metals are susceptible to specific chemical species, and some alloys are susceptible to SCC in one environment while others are more resistant.

Increasing the temperature of a system often works to accelerate the rate of SCC. The presence of chlorides or oxygen in the environment can also significantly influence the occurrence and rate of SCC. SCC is a concern in alloys that produce a surface film in certain environments, since the film may protect the alloy from other forms of corrosion, but not SCC. Some specific environments that can cause SCC of certain metals are listed in Table 25.

<p align="center">Table 25   Environments that May Cause Stress Corrosion of Metals[12]</p>

Material	Environment
Aluminum alloys	$NaCl$-H_2O_2 solutions
	$NaCl$ solutions
	Seawater
	Air, water vapor
Copper Alloys	Ammonia vapors and solutions
	Amines
	Water, water vapor
Gold Alloys	$FeCl_3$ solutions
	Acetic acid-salt solutions
Inconel	Caustic soda solutions
Lead	Lead acetate solutions
Magnesium alloys	$NaCl$-K_2CrO_4 solutions
	Rural and coastal atmospheres
	Seawater
	Distilled water
Monel	Fused caustic soda
	Hydrofluoric acid
	Hydrofluorosilicic acid
Nickel	Fused caustic soda
Ordinary steels	$NaOH$ solutions
	$NaOH$-Na_2SiO_2 solutions
	Calcium, ammonium, and sodium nitrate solutions
	Mixed acids (H_2SO_4-HNO_3)
	HCN solutions
	Acidic H_2S solutions
	Seawater
	Molten Na-Pb alloys
Stainless steels	Acid chloride solutions such as $MgCl_2$ and $BaCl_2$
	$NaCl$-H_2O_2 solutions
	Seawater
	H_2S
	$NaOH$-H_2S solutions
	Condensing steam from chloride waters
Titanium alloys	Red fuming nitric acid, seawater, N_2O_4, methanol-HCl

4.8.2   Managing Stress Corrosion Cracking

There are several methods that may be used to minimize the risk of SCC. Some of these methods include:

Choose a material that is resistant to SCC.

Employ proper design features for the anticipated forms of corrosion. Corrosion pits may produce crack initiation sites.

Minimize stresses including thermal stresses.

Environment modifications (pH, oxygen content).

Use surface treatments (shot peening, laser treatments) which increase the surface resistance to SCC.

Any barrier coatings will deter SCC as long as it remains intact.

Reduce exposure of end grains (i.e. end grains can act as initiation sites for cracking because of preferential corrosion and/or a local stress concentration).

4.9   Other Forms of Corrosion

Not all types of corrosion can be easily classified as one of the eight major forms of corrosion described in the preceding sections. Therefore, some of the less common or more unique forms of corrosion are described in the following sections. These forms of corrosion may, in some instances, be considered as a subgroup of one of the eight major forms.

4.9.1   Corrosion Fatigue

Corrosion fatigue is a decrease in fatigue strength due to the effects of corrosion. Corrosion fatigue cracking differs from SCC and hydrogen induced cracking in that the applied stresses are cyclic rather than static. Fatigue cracking is often characterized by "beach marks" or striation patterns which are perpendicular to the crack propagation direction, as shown in Figure 32. Both the stress required for crack initiation and propagation can be lower in corrosive environments. Factors influencing corrosion fatigue include material strength, fracture toughness, and environmental conditions. There are two primary material properties used to assess fatigue, the number of cycles to failure for an applied stress level or the crack growth per cycle for a stress intensity factor.

Figure 32   Characteristic Fatigue Striation Pattern[15]

4.9.1.1   Factors Affecting Corrosion Fatigue

The selection of materials for increased fracture toughness involves a trade-off with strength. Increased strength normally reduces fracture toughness and vice versa. One method to enhance fracture toughness while maintaining strength is reducing the metal's average grain size. Additionally, highly polished surfaces resist crack initiation better as do lower temperatures. There are a couple of surface treatments that may be used to induce residual compressive stresses, thereby increasing fatigue strength. They include shot peening, laser shock peening, and recently, low plasticity burnishing. The metals' particular susceptibility to environmental conditions, as always, is a factor.

4.9.1.2   Stress-Life (S-N) Data

One type of reported fatigue data is stress-life or S-N curves, which plot the stress amplitude versus the number of cycles to failure. This follows the empirical relationship

$$\frac{\Delta\sigma}{2} = \sigma_f' \left(2N_f\right)^b$$

<div align="right">Equation 10</div>

where,

$\Delta\sigma$ = change in stress

σ_f' = fatigue strength coefficient

N_f = number of cycles to failure

b = fatigue strength exponent

In a fully reversed, constant stress amplitude fatigue test, $\frac{\Delta\sigma}{2} = \sigma_a$, the stress amplitude.
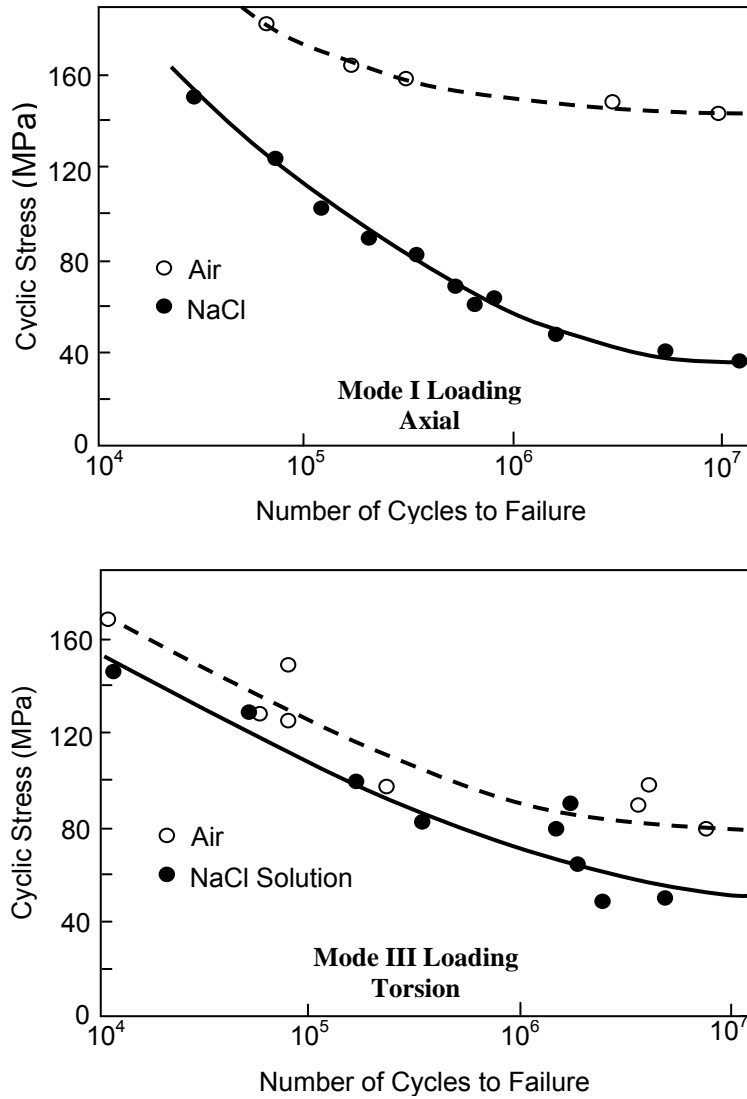
Figure 33   S-N Data for 7075-T6 in Air and NaCl Solution[16]

4.9.1.3   Fatigue Crack Growth Data

Information on fatigue can also be found in the form of crack growth plots. The relation in this case is

$$\frac{da}{dN} = C(\Delta K)^m$$

Equation 11

$$K = \sigma\sqrt{\pi a}$$

where,

        a = one half crack length
        N = number of cycles
        K = stress intensity factor
        σ = stress amplitude
        C,m = empirical constants

There are three types of fatigue crack growth behavior as depicted in Figure 34. Type A exists for materials affected by the corrosive environment for crack initiation and crack growth. Type B behavior exists for materials where no environmental effect exists below the stress intensity threshold fro SCC. Type C is a combination of types A and B. Aluminum alloys in seawater follow type A behavior as can be seen in Figure 35.

Type A   Type B   Type C
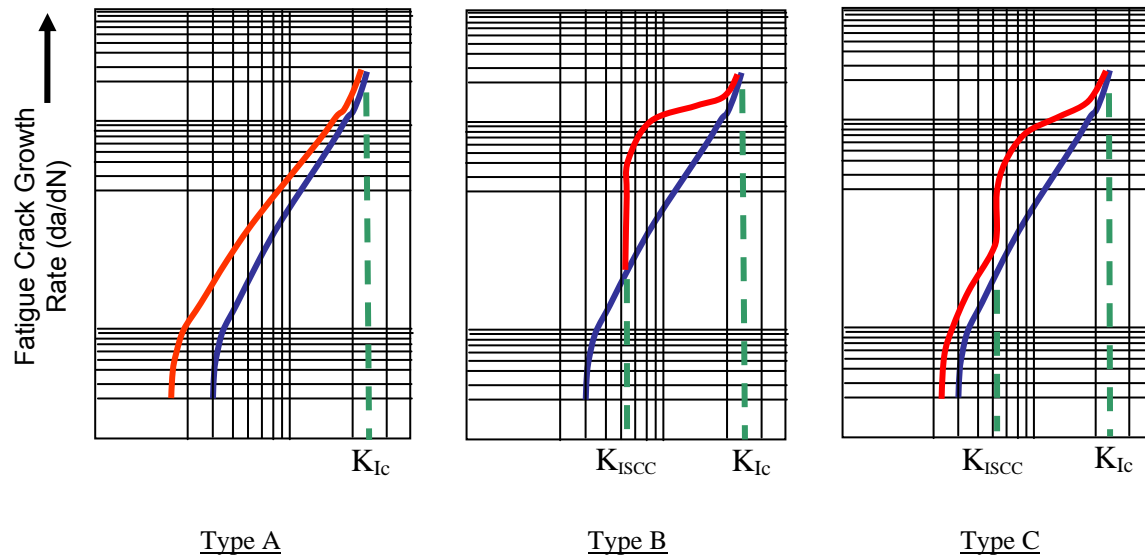
Figure 34   Types of Fatigue Crack Growth Rates

4.9.1.4   Managing Corrosion Fatigue

Methods to deter corrosion fatigue include the following:

- Employ designs which minimize stresses to the components

- Choose heat treatments that reduce residual stresses

- Use surface treatments that enhance corrosion fatigue resistance such as shot peening or laser treatments (Section 7.2)

- Use barrier coatings or corrosion preventive compounds to block corrosive species from the metal.
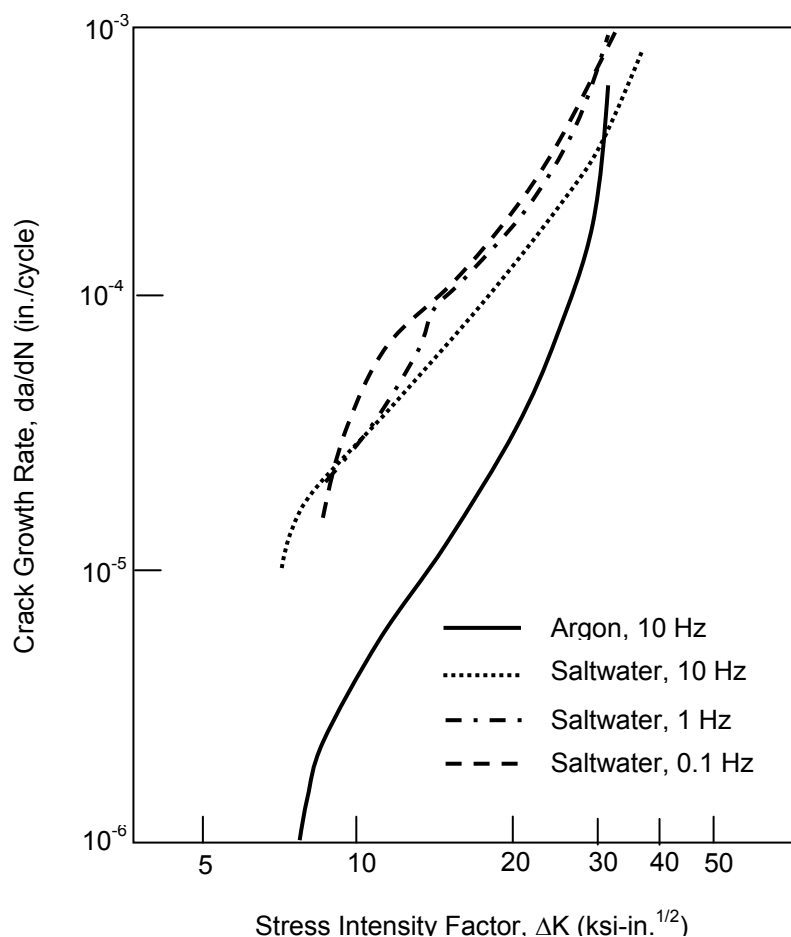
Figure 35   Crack Growth rates for 7075-T6[17]

4.9.2   Fretting Corrosion

Fretting corrosion occurs where two metals are in contact and there is a relatively small motion between the materials. It can be thought of as the combination of wear and a corrosive environment. This process usually presents itself in material interfaces not designed to be in motion with respect to each other. Typical applications that have produced fretting corrosion are motor shafts and electrical contacts. In the case of motor shafts, machinery vibration causes fretting and usually results in decreased fatigue life, known as fretting fatigue. Proper alignment of the rotating shafts is critical to reducing fretting fatigue failures. A second form of fretting corrosion appears in electrical contacts where thermal expansion and contraction cycles result in degradation of the contacting materials. Electrical contacts are most often coated with a noble metal, which are resistant to fretting corrosion. Cyclic motion, however, can cause wear and failure of the coating leaving the base metal vulnerable to fretting corrosion and other forms of attack. Once the base metal is exposed, the formation of highly resistive oxides occurs resulting in intermittent or open electrical circuits. Fretting corrosion is often undetected due to the nature of its existence in hidden material interfaces. The best way to mitigate fretting corrosion is to be knowledgeable of the typical material combinations and applications where it occurs and the methods used to combat it.

Factors contributing to fretting corrosion include contact conditions, environmental conditions, and materials properties.[18]   These factors all interact to produce fretting corrosion or fretting fatigue, as represented in Figure 36.
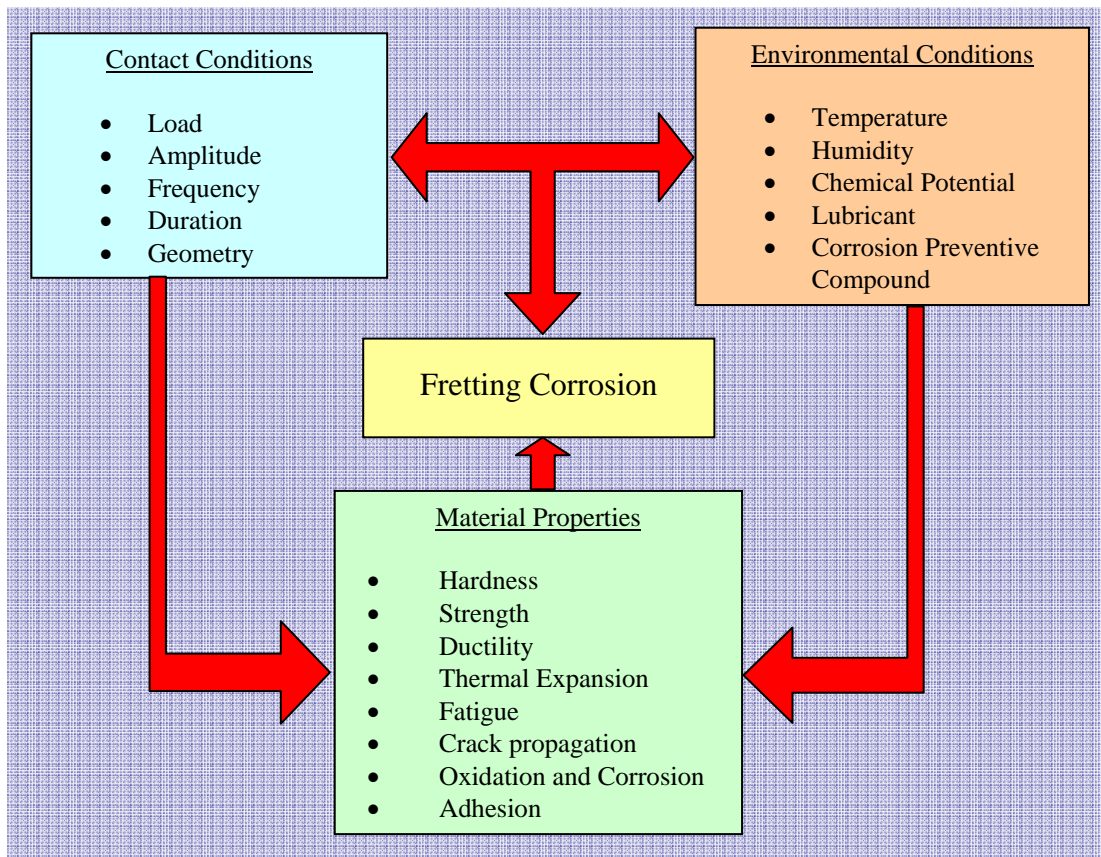
Figure 36   Contributing Factors to Fretting Corrosion[18]

4.9.2.1   Metals' Susceptibilities to Fretting Corrosion

The susceptibilities of some material combinations to fretting are listed in Table 26.

4.9.2.2   Managing Fretting Corrosion

Methods used to reduce fretting corrosion include the following:

- Soft metal against hard metal contacts
- Roughen surface to reduce slippage
- Increase load to reduce relative motion
- Low viscosity fluids in combination with phosphate treated surfaces
- Increase surface hardness of contacting metals
- Use one metal with a low coefficient of friction
- Use corrosion preventive compounds on electrical contacts

Table 26   Resistance to Fretting Corrosion of Various Material Couples under Dry Conditions[19]

High Resistance	Medium Resistance	Low Resistance
Lead against Steel	Cadmium against Steel	Steel against Steel
Silver Plate against Steel	Zinc against Steel	Nickel against Steel
Silver Plate against Aluminum Plate	Copper Alloys against Steel	Aluminum against Steel
Steel with a conversion coating against Steel	Zinc against Aluminum	Antimony Plate against Steel
	Copper Plate against Aluminum	Tin against Steel
	Nickel Plate against Aluminum	Aluminum against Aluminum
	Iron Plate against Aluminum	Zinc-Plated Steel on Aluminum
	Silver Plate against Aluminum	Iron-Plated Steel against Aluminum

4.9.3   Hydrogen Damage

There are a number of different forms of hydrogen damage to metallic materials, resulting from the combined factors of hydrogen and residual or tensile stresses. Hydrogen damage can result in cracking, embrittlement, loss of ductility, blistering and flaking, and also microperforation.

4.9.3.1   Hydrogen Induced Cracking

Hydrogen induced cracking (HIC) refers to the cracking of a ductile alloy when under constant stress and where hydrogen gas is present. Hydrogen is absorbed into areas of high triaxial stress producing the observed damage.

4.9.3.2   Hydrogen Embrittlement

Hydrogen embrittlement is the brittle fracture of a ductile alloy during plastic deformation in a hydrogen gas containing environment.

4.9.3.3   Loss of Tensile Ductility

The loss of tensile ductility occurs with metals exposed to hydrogen which results in a significant reduction in elongation and reduction in area. It is most often observed in low strength alloys and has been witnessed in steels, stainless steels, aluminum alloys, nickel alloys, and titanium alloys.

4.9.3.4   High Temperature Hydrogen Attack

High pressure hydrogen will attack carbon and low-alloy steels at high temperatures. The hydrogen will diffuse into the metal and react with carbon resulting in the formation of methane. This in turn results in decarburization of the alloy and possibly cracks formation.

4.9.3.5   Blistering

Blistering occurs primarily in low strength metals. It is a result of atomic hydrogen diffusion into defect areas of the alloy. The monotonic atoms combine into gas molecules in voids within the metal. Then, the high pressure of H_2 entrapped within the metal causes the material to blister

or rupture. This form of attack has been observed in low strength steels exposed to H_2S or when cleaned in pickling baths.

4.9.3.6 Shatter Cracks, Flaking, and Fish Eyes

These forms of hydrogen damage are similar to blistering and are seen primarily during processing. Hydrogen is more soluble at the melting temperatures of metals allowing it to enter defect areas. The decreased solubility of hydrogen when cooled then produces the damage features.

4.9.3.7 Microperforation

Microperforation has been seen in steels in a high pressure hydrogen and room temperature environment. The hydrogen produces fissures in steel alloys such that gases and liquids can permeate the material.

4.9.3.8 Degradation in Flow Properties

An increase in creep rates occurs in iron alloys and steels under ambient conditions in hydrogen environments, and in several alloys at elevated temperatures.

4.9.3.9 Hydride Formation

The precipitation of metal hydride phases in magnesium, tantalum, niobium, vanadium, uranium, zirconium, titanium, and their alloys, in the presence of hydrogen produces a degradation of mechanical properties and cracking.

4.9.3.10 Metals' Susceptible to Hydrogen Damage

Table 27 lists susceptible metals to the various types of hydrogen attack..

Table 27   Metals' Susceptibilities to Hydrogen Damage[20]

Hydrogen Induced Cracking	Hydrogen Embrittlement	Loss in Tensile Ductility	High Temperature Hydrogen Attack	Blistering
Steels Nickel-alloys metastable stainless steel titanium-alloys	Carbon and low-alloy steels	Steels nickel-alloys Be-Cu bronze Aluminum-alloys	Carbon and low-alloy steels	Steels Copper Aluminum
Shatter Cracks, Flakes, Fisheyes	**Micro-Perforation**		**Degradation in Flow Properties**	**Metal Hydride Formation**
Steels (forgings and castings)	Steels (compressors)		Iron Steels Nickel-alloys	V Nb Ta Ti Zr U

4.9.3.11   Managing Hydrogen Damage

Methods to deter hydrogen damage are to:

- Limit hydrogen introduced into the metal during processing.

- Limit hydrogen in the operating environment.

- Structural designs to reduce stresses (below threshold for subcritical crack growth in a given environment)

- Use barrier coatings

- Use low hydrogen welding rods

4.9.4   High Temperature Corrosion

High temperature corrosion is an attack on a metal at elevated temperatures in a gaseous environment rather than in a liquid. The most prominent high temperature corrosion reaction is oxidation, although sulfidation and carburization may also occur. Most metals exposed to a high temperature oxidative environment will produce an oxide scale layer which protects the metal from further corrosion. It uniformly covers the entire surface. Ionic transport through the scale is the rate controlling process. The corrosion rate will normally decrease after the scale is produced following a parabolic relationship with time. In severe corrosive environments where a protective scale cannot form, the corrosion rate will follow a more linear path.

Sulfidation occurs when the concentration of sulfur gas is high enough such a sulfide layer forms. Sulfides are less stable and grow much faster than oxides. As a result, sulfides react more readily with metals and penetrate deeper into the metal. They are replaced with the more stable oxides as reactions continue to occur. It is preferred in such environments to have a protective oxide scale first produced, which then protects the metal against subsequent sulfidation.

Hot corrosion is a term describing the high temperature attack of gas turbine engine components in the path of hot gases. It is a sulfidation process involving the formation of condensed salts containing sodium sulfate and/or potassium sulfate. Increasing the chromium content in the metal alloys improves the corrosion resistance but also results in decreased strength.

Carburization is a rare form of high temperature corrosion where carbon atoms are absorbed into a metals' surface. It only occurs in environments with a very low oxygen partial pressure. Austenitic stainless steels are susceptible under such conditions due to the high solubility of carbon in austenite. Alloying studies to reduce carburization have shown that silicon, niobium, tungsten, titanium, and the rare earth metals increase resistance. Elements which increase damage include lead, molybdenum, boron, cobalt, and zirconium.

4.9.4.1   Metals' Susceptible to High Temperature Corrosion

Although high temperature corrosion testing, especially on superalloy materials for gas turbine applications, has been conducted, no qualitative relationship has been determined. Materials are selected for corrosion resistance dependent upon their comparative rates of attack from tests and from field experience.

4.9.4.2   Managing High Temperature Corrosion

Methods to reduce high temperature corrosion include:

- Proper metal selection.

- Change in operating conditions.

- Structural designs to limit corrosion.

- High temperature barrier coatings (ceramics)

4.9.5   Exfoliation

Exfoliation corrosion is considered a form of intergranular corrosion that attacks metals which have been mechanically deformed, primarily by extrusion or rolling, producing elongated grains directionally aligned. Most often, the attack is initiated at exposed endgrains, as has been the case with aircraft skins around fasteners see Figure 37. This form of corrosion is most evident in some of the aluminum alloys and is shown in Figure 38. Metals susceptible to exfoliation corrosion are aggressively attacked in environments corrosive to that particular metal. As an example, AA 2024-T4 is known to perform well in urban type environments, but is severely attacked in marine environments.
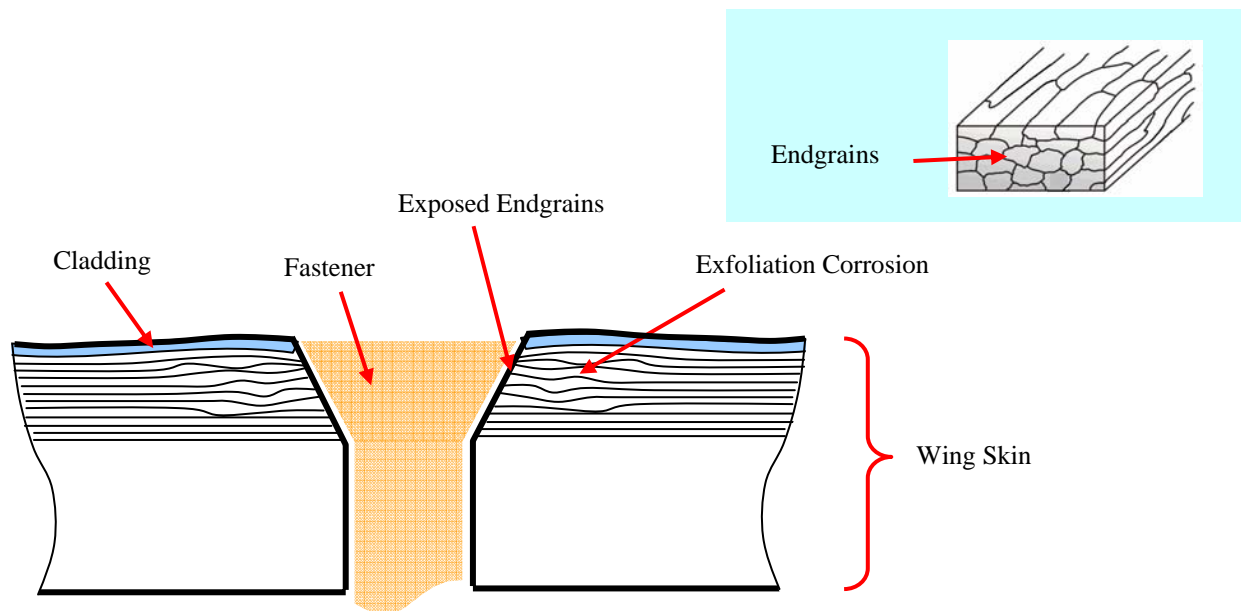
Figure 37   Exfoliation Corrosion Initiated at Endgrains

Figure 38   Exfoliation of an Aluminum Alloy in a Marine Environment[2]

4.9.5.1   Managing Exfoliation Corrosion

As with intergranular corrosion, the proper selection of alloy and heat treatment to avoid precipitation at grain boundaries is the primary method to combat exfoliation. Reducing the area of endgrain surfaces will limit the initiation of attack, as well as the use of barrier coatings.

4.9.6   Microbiological Corrosion

MIC is actually not a form of corrosion, but rather is a process that can influence and even initiate corrosion. It can accelerate most forms of corrosion; including uniform corrosion, pitting corrosion, crevice corrosion, galvanic corrosion, intergranular corrosion, dealloying, and stress corrosion cracking. In fact, if unfamiliar with MIC, some corrosion problems may be misdiagnosed as conventional chloride induced corrosion. One prominent indicator of MIC is a higher rate of attack than one would normally expect. MIC can affect numerous systems, and can be found virtually anyplace where aqueous environments exist. It is not exclusive to water-based systems, occurring in fuel and lubrication systems as well. Figure 28 lists applications where MIC has been found to be prominent while Figure 29 shows one such location.

Table 28   Systems with Persistent MIC Problems[21]

Application/System	Problem Components/Areas	Microorganisms
Pipelines/storage tanks (water, wastewater, gas, oil)	Stagnant areas in the interior Exterior of buried pipelines and tanks, especially in wet clay environments.	Aerobic and anaerobic acid producers Sulfur reducing bacteria Iron/manganese oxidizing bacteria Sulfur oxidizing bacteria
Cooling systems	Cooling towers Heat exchangers Storage tanks	Aerobic and anaerobic bacteria Metal oxidizing bacteria Slime forming bacteria Algae Fungi
Docks, piers, and other aquatic structures	Splash zone Just below low tide	Sulfate reducing bacteria
Vehicle fuel tanks	Stagnant areas	Fungi
Power generation plants	Heat exchangers Condensers	Aerobic and anaerobic bacteria Sulfate reducing bacteria Metal oxidizing bacteria
Fire sprinkler systems	Stagnant areas	Anaerobic bacteria Sulfate reducing bacteria

Figure 39   Interior of a Ballast Tank on a Navy Ship[22]

4.9.6.1   Types of Microorganisms

The types of microorganisms with species attributable to MIC include algae, fungi, and bacteria.[23] Algae produce oxygen in the presence of light (photosynthesis) and consume oxygen in darkness. They can be found in most any aquatic environment ranging from freshwater to concentrated salt water. The availability of oxygen has been found to be a major factor in corrosion of metals in saltwater environments. Algae flourish in temperatures of 32 - 104°F and pH levels of 5.5 – 9.0. Fungi consist of mycelium structures which are an outgrowth of a single cell or spore. Mycelia are immobile, but can grow to reach macroscopic dimensions. Fungi are most often found in soils, although some species are capable of living in water environments. They metabolize organic matter, producing organic acids.

Bacteria are generally classified by their affinity to oxygen. Aerobic species require oxygen to metabolize while anaerobic species require a lack of oxygen to do the same. Facultative bacteria can grow in either environment, although they prefer aerobic conditions. Microaerophilic bacteria require low concentrations of oxygen. Oddly enough, aerobic and anaerobic organisms have often been found to co-exist in the same location. This is because aerobic species deplete the immediate surroundings of oxygen creating an ideal environment for anaerobes. Bacteria are further classified by shape into spherical (bacillus), rod (coccus), comma (vibrio), and filamentous (myces) species. Figure 40 is an example of rod-shaped bacteria observed using transmission electron microscopy.
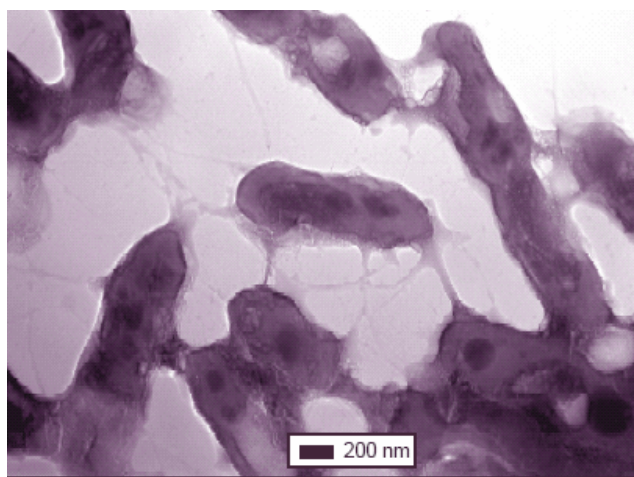
Figure 40   Rod-Shaped Pseudomonas Bacteria[24]

Microorganisms in the planktonic state refer to those organisms floating freely in the aqueous environment or in air. They can resist harsh environments including acids, alcohols, and disinfectants, drying, freezing, and boiling.[25] Some spores have the ability to last hundreds of years and then germinate once favorable conditions exist. Microorganisms in the sessile state are those that have attached themselves to a surface and have developed a protective membrane, collectively called a biofilm. Microorganisms have the ability to reproduce quickly; some doubling in as little as 18 minutes. When left untreated, they can rapidly colonize in stagnant aqueous environments, potentially introducing a highly active corrosion cell.

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4.9.6.2   Microorganisms that Accelerate Corrosion

Once a microorganism forms a biofilm on a material's surface, a microenvironment is created that is dramatically different from the bulk surroundings. Changes in pH, dissolved oxygen, and organic and inorganic compounds in the microenvironment can lead to electrochemical reactions which increase corrosion rates. Microorganisms may also produce hydrogen which can promote hydrogen damage in metals. Most microorganisms form an extracellular membrane which protects the organism from toxic chemicals and allows nutrients to filter through.[25] Biofilms are resistant to many chemicals by virtue of their protective membrane and ability to breakdown numerous compounds. They are significantly more resistant to biocides (chemicals used to kill microorganisms) than planktonic organisms. Some bacteria even metabolize corrosion inhibitors, such as aliphatic amines and nitrites, decreasing the inhibitor's ability to control corrosion. Microorganisms' metabolic reactions attributable to metallic corrosion involve sulfide production, acid production, ammonia production, metal deposition, and metal oxidation and reduction. Several groups of microorganisms have been attributed to MIC, and are listed below.[26] Following these recognized forms; Table 29 lists some specific microorganisms within these categories, along with their characteristics.

Sulfate Reducing Bacteria (SRB)

Sulfate reducing bacteria are anaerobic microorganisms that have been found to be involved with numerous MIC problems affecting a variety of systems and alloys. They can survive in an aerobic environment for a period of time until finding a compatible environment. SRB chemically reduce sulfates to sulfides, producing compounds such as hydrogen sulfide (H_2S), or iron sulfide (Fe_2S) in the case of ferrous metals. The most common strains exist in the temperature range of 25 - 35ºC, although there are some that can function well at temperatures of 60ºC. They can be detected through the presence of black precipitates in the liquid media or deposited on surfaces, as well as a characteristic hydrogen sulfide smell.

Sulfur/Sulfide Oxidizing Bacteria (SOB)

Sulfide oxidizing bacteria are an aerobic species which oxidize sulfide or elemental sulfur into sulfates. Some species oxidize sulfur into sulfuric acid (H_2SO_4) leading to a highly acidic (pH $\leq$ 1) microenvironment. The high acidity has been associated with the degradation of coating materials in a number of applications. They are primarily found in mineral deposits and are common in wastewater systems. SRB is often found in conjunction with SOB.

Iron/Manganese Oxidizing Bacteria

Iron and manganese oxidizing bacteria have been found in conjunction with MIC, and are typically located over corrosion pits on steels. Some species are known to accumulate iron or manganese compounds resulting from the oxidation process. The higher concentration of manganese in biofilms has been attributed to corrosion of ferrous alloys including pitting of stainless steels in treated water systems. Iron tubercles have also been observed to form as a result of the oxidation process (Figure 41).

Table 29   Common Microorganisms Found in Conjunction with MIC[27]

	Genus or Species	pH	Temperature (°F)	Oxygen Requirement	Metals Affected	Metabolic Process
Bacteria	Desulfovibrio	4-8	50-105	Anaerobic	Iron and steel, stainless steels, aluminum, zinc, copper alloys	Use hydrogen in reducing SO_4^{2-} to S^{2-} and H_2S; promote formation of sulfide films
	Desulfotomaculum	6-8	50-105 (some at 115-165)	Anaerobic	Iron and steel, stainless steels	Reduce SO_4^{2-} to S^{2-} and H_2S
	Desulfomonas	-	50-105	Anaerobic	Iron and steel	Reduce SO_4^{2-} to S^{2-} and H_2S.
	Acidthiobacillus thiooxidans	0.5-8	50-105	Aerobic	Iron and steel, copper alloys, concrete	Oxidizes sulfur and sulfides to form H_2SO_4; damages protective coatings
	Acidithiobacillus ferrooxidans	1-7	50-105	Aerobic	Iron and steel	Oxidizes ferrous (Fe^{2+}) to ferric (Fe^{3+})
	Gallionella	7-10	70-105	Aerobic	Iron and steel, stainless steels	Oxidizes ferrous to ferric ions and manganous (Mn^{2+}) to manganic (Mn^{3+}) ions; promotes tubercule formation
	Siderocapsa	-	-	Microaerophilic	Iron and carbon steel	Oxidizes iron
	Leptothrix	6.5-9	50-95	Aerobic	Iron and steel	Oxidizes ferrous to ferric ions and manganous to manganic ions
	Sphaerotilus	7-10	70-105	Aerobic	Iron and steel, stainless steels	Oxidizes ferrous to ferric ions and manganous to manganic ions; promotes tubercule formation
	Sphaerotilus natans	-	-	-	Aluminum alloys	-
	Pseudomonas	4-9	70-105	Aerobic	Iron and steel, stainless steels	Some strains reduce Fe^{3+} to Fe^{2+}
	Pseudomonas aeruginosa	4-8	70-105	Aerobic	Aluminum alloys	-
Fungi	Cladosporium resinae	3-7	50-115 (best at 85-95)	-	Aluminum alloys	Produces organic acids when metabolizing certain fuel constituents

Figure 41   Tubercles as a Result of MIC (courtesy of Metallurgical Technologies, Inc.) [28]

Slime Forming Bacteria

Slime forming bacteria are aerobic organisms which develop polysaccharide "slime" on the exterior of cells. The slime controls permeation of nutrients to the cells and may breakdown various substances, including biocides. Slime formers have been responsible for the decreased performance of heat exchangers as well as clogging of fuel lines and filters. They can prevent oxygen from reaching the underlying metal surface, creating an environment suitable for anaerobic organisms.

Organic Acid Producing Bacteria

Some anaerobic organisms also produce organic acids. These bacteria are more apt to be found in closed systems including gas transmission lines and sometimes closed water systems.

Acid Producing Fungi

Some fungi produce organic acids which attack iron and aluminum alloys. Like slime formers, they can create environments suitable for anaerobic species.   These organisms have been attributed to the widespread corrosion problems observed in aluminum fuel tanks in aircraft.

4.9.6.3   Metals Affected by MIC

Since MIC is a mechanism that accelerates corrosion, it should be expected to occur more often in metal alloys with susceptibilities to the various forms of corrosion, and in environments conducive to biological activity. Metals used in the applications listed in Table 1, and thus exposed to microbial activity and the potential of MIC, include mild steels, stainless steels, copper alloys, nickel alloys and titanium alloys. In general, mild steels can exhibit everything from uniform corrosion to environmentally assisted cracking, while the remaining alloys usually only show localized forms. Mild steels, stainless steels, aluminum, copper, and nickel alloys all have shown effects of MIC, while titanium alloys have been found to be virtually resistant to MIC under ambient conditions.

Mild Steels

MIC problems have been widely documented in piping systems, storage tanks, cooling towers, and aquatic structures. Mild steels are widely used in these applications due to their low cost, but are one of the most readily corroded metals. Mild steels are normally coated for corrosion

protection, while cathodic protection may also be used for select applications. Galvanization (zinc coating) is commonly used to protect steel in atmospheric environments. Bituminous coal tar and asphalt dip coatings are often used on the exterior of buried pipelines and tanks, while polymeric coatings are used for atmospheric and water environments. However, biofilms tend to form at flaws in the coating surfaces. Furthermore, acid producing microorganisms have been found to dissolve zinc and some polymeric coatings.[29] Numerous cases have also been documented where microorganisms caused debonding of coatings from the underlying metal. Underneath the delaminated coating in turn, creates an ideal environment for further microbial growth.

Poor quality water systems and components with areas that accumulate stagnant water/debris are prone to MIC. In some extreme cases, untreated water left stagnant within mild steel piping has caused uniform corrosion throughout the low lying areas. This has been seen to occur in underground pipes that have been left unused for periods of time.[29] Many power plant piping failures have been found to be the result of introducing untreated water into a system. SRB has been the primary culprit in such cases. A change to a more corrosion resistant material is not always the answer when it comes to solving MIC problems. For example, an upgrade from carbon steel to stainless steel in a nuclear power plant caused a change in MIC problems that in some instances were even more severe. SRB has also been found in conjunction with underdeposit corrosion occurring in cooling towers. Wet soils containing clay have played a major role in the occurrence of underground MIC problems. Under such conditions, the exterior of underground piping and storage tanks have experienced coating delamination and corrosion as a result of biofilm growth.

Stainless Steels

Stainless steels have suffered MIC problems in the same type of scenarios as mild steels - primarily in locations where water accumulates. There are two notable problems that have surfaced with stainless steel MIC. One is an accelerated corrosion rate, primarily through pitting or crevice corrosion that occurs in low lying areas, joints, and corner locations. Stainless steel tanks and piping systems are sometimes hydrotested subsequent to manufacture and prior to field use. Several cases of severe MIC have been documented whereby hydrotesting using well water was performed, and the product was then stored for a period of time before being placed into service.[29] The tanks and piping were not adequately dried, nor was a biocide used to deter biofilm growth. In one particular case, a 304 stainless steel pipeline for freshwater service, failed 15 months after being hydrotested.[30] A second MIC problem discovered with stainless steels occurs adjacent to weldments. Microorganisms readily attack areas around welds due to the inhomogeneous nature of the region. In one case, perforation occurred in a 0.2 inch diameter 316L stainless steel pipe adjacent to a welded seam after four months in service under intermittent flow conditions.[31] Stainless steels containing 6% molybdenum or greater, have been found to be virtually resistant to MIC.[29]

Aluminum Alloys

The major applications where MIC has attacked aluminum alloys have been in fuel storage tanks and aircraft fuel tanks.[29] MIC problems exist in the low-lying areas of tanks and at water–fuel interfaces. Contaminants in fuels, such as surfactants and water soluble salts, have largely contributed to the formation of biofilms in these systems. Fungi and bacteria have been found to be the main culprits. Cladosporium resinae, a fungus, has widely been attributed to corrosion of

aircraft fuel tanks. Its presence decreases the pH to around 3-4, which can attack the protective coatings and underlying metal. Pseudomonas aeruginosa and Candida species are also likely to be found in conjunction with MIC of aluminum fuel tanks.

Additionally, heavy fungal growth on interior surfaces of helicopters has occurred subsequent to depot maintenance and prior to returned field use.[32] Fungal growth had been reported in passenger areas of the H-53 helicopter and was therefore slated for cleaning during refurbishment. Fungi could be found on virtually all interior surfaces of the helicopter. The surfaces were cleaned with 100% isopropanol, treated with a biocide, followed by application of a corrosion preventive compound. The procedure removed most of the microorganisms present and was effective at killing spores. However, some biofilms remained, which rapidly reproduced before the aircraft was even returned to service.

Copper Alloys

Copper alloys find use in seawater piping systems and heat exchangers, which are susceptible to MIC. Microbial products that can be harmful to copper alloys include CO_2, H_2S, NH_3, organic and inorganic acids, and sulfides.[29] MIC observed in copper alloys includes pitting corrosion, dealloying and stress-corrosion cracking. Higher alloying content in copper usually results in a lower corrosion resistance. Although MIC has been found in both, more problems have been documented with 70/30 than with 90/10 Cu/Ni alloys. MIC has also been documented in Admiralty brass (Cu-30Zn-1Sn), aluminum brass (Cu-20Zn-2Al), and aluminum bronze (Cu-7Al-2.5Fe). Ammonia and sulfides have gained considerable attention as compounds that are corrosive to copper alloys. Admiralty brass tubes have been found to suffer stress-corrosion cracking in the presence of ammonia. Seawater that is high in sulfide content, has caused pitting and stress-corrosion cracking in copper alloys. SRB has also been known to attack copper alloys causing dealloying of nickel or zinc in some cases.

Nickel Alloys

Nickel alloys are used in high velocity water environments including evaporators, heat exchangers, pumps, valves, and turbines blades, as they generally have a higher resistance to erosive wear than copper alloys.[29] However, some nickel alloys are susceptible to pitting and crevice attack under stagnant water conditions, so that downtime and unused periods can lead to potential MIC problems. Monel 400 (66.5Ni-31.5Cu-1.25Fe) has been found to be susceptible to underdeposit MIC. Pitting corrosion, intergranular corrosion, and dealloying of nickel have all been observed with this alloy in the presence of SRB. Ni-Cr alloys have been found to be virtually resistant to MIC.

4.9.6.4 Monitoring/Detection Methods

Early detection of potential MIC is crucial to the prevention of equipment failure and extensive maintenance. The most common detection methods involve sampling bulk liquids from within the system and monitoring physical, chemical, and biological characteristics. The goal is to identify favorable conditions for biofilm formation and growth, so that the internal environment may be adjusted as appropriate. Visual inspections of accessible areas should also be performed on a routine basis. Additional methods that may be utilized include coupon monitoring, electrochemical sensor and biosensor techniques.

Monitoring equipment is available for measuring a number of properties of the bulk system. A common practice has been to monitor temperature, pH, conductivity, and total dissolved solids directly from the operating system, while taking samples for portable or laboratory testing methods to evaluate dissolved gases, bacteria counts, and for bacteria identification.[21] Bacteria counting, via cultured growth, may be helpful, but strict conditions must be followed to produce meaningful results. The most important factor in bacterial counts is observing changes in trends rather than in actual numbers. Consistency is crucial where deviations in sample location, temperature, growing media, growth time, and even changes in technicians can affect results. A strict schedule must also be maintained. Changes in bacteria counts are used to adjust biocide usage and may also be indicative of biofilm growth in the case of differences in counts across a system. Bacteria cultures can also be used to identify specific species present (Figure 42). Direct bacteria counts can be performed using a microscope to inspect bacteria which have been placed onto a slide and may also be stained for viewing, as shown in Figure 43. Visual inspections should be performed on exposed surfaces where algae and fungal growth can occur, and on surfaces exposed during maintenance procedures. The presence of SRB can be detected by observing black particles in the liquid media and/or deposited on surfaces, a result of iron sulfide and/or copper sulfide formation, or a distinct hydrogen sulfide odor.[33] Fluorescent dyes can be used to enhance visual detection, as biofilms absorb some of the dye whereby an ultraviolet light is then used to expose the microorganisms.

Figure 42   Bacteria Culture[34]

Figure 43   Inspection of Bacteria on a Stained Microscope Slide[35]

Coupons have been found quite useful in detecting MIC, especially when used in conjunction with additional monitoring techniques. Coupons are small metal samples placed within the system and periodically extracted to measure corrosion rates through weight loss and possibly to collect microorganisms from biofilms on the coupon for identification. Proper placement of the coupons within the system plays a key role in MIC monitoring and detection. Coupons should be placed in locations where MIC is likely to occur. Electrochemical sensing techniques, such as electrical impedance spectroscopy and electrochemical noise, are other means of detecting MIC. Electrochemical sensors detect characteristics of corrosion reactions, such as changes in electrical conductivity. As with coupons, strategic placement of the sensors in the systems is crucial to detecting MIC.

One type of sensor designed specifically for biofilm detection uses a probe that attracts microbial growth.[36] Utilizing experience of the electrochemical conditions under which biofilms occur, probes have been developed that replicate these preferred conditions. The sensor then alerts operators when biofilm activity is present. Sensors should ideally be placed in areas where biofilm growth is more likely. Another method that may be used specifically to detect microorganisms in water systems is the use of fluorogenic bioreporters.[37] These are compounds (dyes) that change their fluorescence upon interaction with microorganisms. Activity is determined by the ratio of fluorescence of the reacted dye, extracted from the system or measured in-service, to the unreacted dye. The ratio increases with biological activity and can be used to effectively regulate the use of biocides. This method however, does not distinguish between planktonic and sessile organisms. Thus, problems could be growing in the system without being detected.

4.9.6.5   Mitigation Methods

Clearly, the best way to prevent MIC is to prevent the growth of biofilms altogether. Once a biofilm has formed, it is more resistant to biocides, and can rapidly grow if not completely removed. The emphasis is placed on cleanliness and incorporating established corrosion prevention and control techniques for the various metal alloys and forms of corrosion. Monitoring and detection of microorganisms will effectively guide preventive maintenance procedures.

Cleanliness of systems involves monitoring the quality of water, fuel, or lubricants present in the system. This includes water content in fuel and lubrication systems. Water should be monitored and removed when the content becomes too high. All fluids should be monitored for solid particles and filtered to prevent particle contamination. Contaminants increase the likelihood of biofilms through their use as nutrients. Bacterial counts and biosensing help to adjust the level of biocides introduced to the system. Biocides are widely used and are effective at killing planktonic microorganisms. The cost of biocides is significant however, and along with their toxicity, effective management of biocide use can reduce costs and damaging effects on the environment. Cleanliness also includes scheduled cleaning of exterior components where any debris accumulation has occurred. Non-abrasive cleaning methods are preferred as to not damage coatings. Inspection/cleaning should also be performed on normally inaccessible components that are exposed during maintenance/repair procedures. Designing systems that minimize MIC prone areas and providing accessibility for maintenance as appropriate helps to promote system cleanliness. This involves eliminating stagnant and low-flow areas, minimizing crevices and welds, incorporating filtration, drains, and access ports for treatments, monitoring/sampling, and cleaning.

Established corrosion prevention and control methods that are employed to protect metals from the various forms of corrosion will also help mitigate MIC. This includes designing systems to minimize stagnant water conditions, proper base material and coating selection, possible cathodic protection, sealing crevices and around fasteners, using gaskets to minimize galvanic corrosion, proper heat treatments, and post weld treatments. For underground structures, providing ample drainage by backfilling with gravel or sand will help prevent MIC. In some cases, a change to an alternate material such as PVC piping has greatly reduced underground pipeline corrosion problems. Coatings can be formulated with biocides, though such coatings are not generally used on the interior of systems. Smooth surface finishes with minimized defects are preferred. Research into alternative coatings that may deter MIC has shown polydimethylsiloxane coated 4340 steel to have favorable results.[38] In laboratory tests, the silicone compounds significantly reduced MIC of the steel in a 0.6M NaCl solution over a two year period.

4.9.7   Liquid and Solid Metal Embrittlement

Liquid metal embrittlement (LME) is a brittle fracture of a normally ductile metal when in contact with a liquid metal and stressed in tension. There is no change in the yield behavior of the metal; however, fracture can occur well below the metal's yield strength. The stress required for crack propagation is lower than that for crack initiation. As a result, the crack initiation and propagation are seen instantaneously with a complete fracture of the metal. Fracture surfaces are usually completely covered with the liquid metal. The movement of the liquid metal into the crack is attributed to the rapid crack propagation through the material. In some cases, solid metals at temperatures in the vicinity of their melting points have also been shown to cause embrittlement. This phenomenon has been termed solid metal induced embrittlement (SMIE). Table 30 lists LME interactions of various metals.

Table 30   Liquid Metal Embrittlement Observed in Various Metals[20]

Liquid	Bi	Na	Pb	Sn	Ga	Hg	In	Li
Solid	Al Al alloy Cu Cu alloy Ge	Al Alloy Cu Mg alloy	Al Al alloy Cu Cu alloy Fe alloy Ge Ni Ni alloy Zn	Al alloy Cd Cu alloy Fe alloy Ge Ni alloy Zn	Ag Al Al alloy Cd Cu alloy Fe alloy Ge Sn Zn	Ag Al Al alloy Bi Cu Cu alloy Fe alloy Ni Sn Zn	AL Al alloy Cu alloy Fe alloy Ge Zn	Ag Ag alloy Cu Cu alloy Fe alloy Ni Ni alloy Pd Pd alloy

Liquid	Cd	Cs	Cu	Sb	Te	Ti	Zn
Solid	Al Ge	Cd	Fe Fe alloy	Fe alloy Ge	Fe alloy	Ge	Al alloy Fe alloy Mg alloy

Metals are pure species unless noted otherwise.

Liquid metal embrittlement has been seen in processing environments and a handful of operational applications. Plating some metals, such as cadmium plated titanium or steel can produce embrittlement. Zircalloy tubes in nuclear reactors have been known to be embrittled by liquid and solid cadmium. Lithium causes LME in lithium metal cooled reactors.

4.9.8 Molten Salt Corrosion

Molten salt corrosion is the degradation of metal containers by molten or fused salts. There are two general mechanisms attributed to this form of corrosion. The most common is the oxidation of the metal much like in aqueous environments. The second is the dissolution of the metal. To a lesser extent, all forms of aqueous corrosion have been observed in fused salts.

4.9.8.1   Effects of the More Common Molten Salts on Metals

These effects are summarized in Table 31.

4.9.8.2   Managing Molten Salt Corrosion

Methods to reduce molten salt corrosion include:

- Use materials that form a passive nonsoluble films

- Minimize the entry of oxidizing species

- Lower the temperatures

Table 31   Effects of the More Common Molten Salts on Metals[39]

Molten Salts	Effects
Fluorides	■ prevent/deter the formation of the protective film on metals ■ causes selective leaching of chromium leaving behind voids in some stainless steels and Inconel 600.
Chlorides	■ readily attacks steels, most preferably carbides ■ aluminum coatings for steel are ineffective ■ nickel coatings on steel are beneficial ■ nickel alloys decrease in resistance with an increase in oxygen partial pressure ■ prevents the formation of a protective film on nickel alloys ■ causes selective leaching of chromium from Fe-Ni-Cr alloys
Nitrates	■ plain and low-alloy carbon steels good to 500°C. ■ chromium addition is beneficial ■ hydroxide addition further increases resistance of chromium containing steels ■ never use aluminum alloys to contain nitrates (explosive hazard)
Sulfates	■ high temperature alloys with chromium perform well ■ insufficient chromium content results in severe corrosion ■ metals that do not form protective films will be readily attacked
Carbonates	■ austenitic stainless steels perform well up to 500°C ■ nickel alloys containing chromium useful to 600°C ■ 50% chromium alloys needed for use up to 700°C ■ aluminum coatings on steels good up to 700°C ■ alumina coatings required for higher temperatures ■ nickel coatings are inadequate due to the formation of nickel oxides causing intergranular corrosion
Hydroxides	■ peroxide content controls corrosivity ■ causes selective leaching of chromium in stainless steels ■ nickel alloys are more resistant than stainless steels and unalloyed steels ■ aluminum alloys are more resistant ■ most glass and silica materials are readily attacked

4.9.9   Filiform Corrosion

Filiform corrosion is an attack of a metal substrate material underneath a polymeric film. The corrosion initiation is generally due to a defect in the coating. Corrosive elements to the metal substrate deposit in the defect area causing corrosion of the metal as well as bulging and cracking of the coating. The corrosion tends to spread one-dimensionally in a random manner creating patterns resembling a worm path or tentacles emanating form a point, see Figure 44. There is an associated "head" where the corrosion is preceding and the "tail" where the corrosion originated. Filiform corrosion has been observed on steel cans, aluminum foils and painted aluminum alloys, as well as other lacquered metals. It normally occurs in high humidity ($\geq$ 65% RH) although it may result in lower humidity environments of severe corrosivity. The width of the corrosion paths are in the range of 0.05 – 3 mm depending on the coating material and the corrosivity of the environment.

Figure 44   Filiform Corrosion[2]

4.9.9.1   Managing Filiform Corrosion

Methods that reduce filiform corrosion include the following:

- Use less active metal substrates

- Reduce humidity

- Use zinc primers on steel

- Use multiple coat/paint systems

Other corrosion protection methods can be used, and are discussed in terms of combating corrosion in general in Section 7.0.

4.9.10 Stray-Current Corrosion

Stray-current corrosion is an attack of a metal due to the formation of an electric current through that metal which is unintended. This corrosion form is independent of environmental conditions. A direct current is more damaging than alternating currents. In alternating currents, damage will decrease as frequency increases. A major source of stray-currents is underground power lines. Damage to active-passive metals such as aluminum alloys and stainless steels is greater than that for active metals.

4.9.10.1   Managing Stray-Current Corrosion

The best way to combat stray-current corrosion is to prevent the current using insulation techniques. Coatings will not protect the metal and may even accelerate the attack if a flaw in the coating exists. If the current cannot be prevented, methods to deter corrosion include the following:

- Grounding the Stray Current

- Sacrificial Anodes

- Insulation

4.9.11 Grooving Corrosion in Carbon Steel

Grooving corrosion in carbon steels is a specialized form of corrosion that exists for electric resistance welded piping subsequently exposed to aggressive waters.[40] This welding process produces a redistribution of sulfides along the weld line. The result is a preferred attack in the weld area producing grooves in the material. Post weld heat treatments appear to influence grooving corrosion with temperatures of around 750ºC producing a higher susceptibility and higher temperatures, on the order of 1000ºC, decreasing susceptibility.

5.0   Field Experience with the Corrosion of DoD Assets

Although every system containing metallic components is susceptible to corrosion, the form and rate of corrosion varies depending on several factors including, the type of application, environmental usage conditions, types of metals used, contact between adjacent materials and corrosion protection methods employed. There are many environmental and other factors that affect the rate of corrosion of metals. Some of these factors that influence the corrosion of metals include:[41]

- Temperature
- Humidity
- Heat Treatment
- Surface Condition
- Erosion
- Radiation

- Impurities
- Stress
- Pressure
- Oxygenation Differences
- Concentration Differences
- Biological Growth

This chapter discusses some of these factors and how they affect metallic systems incorporated in specific application areas, for example, aircraft, ships and submarines, ground vehicles, and general structures. Each of these sections describes some of the typical environments that are encountered by these systems, some of the major components that are typically susceptible to corrosion, some of the forms of corrosion that often appear, and in some cases the protection methods used to prevent corrosion.

5.1 Aircraft

Corrosion on aircraft can result in anything from a simple, but unpleasant aesthetic problem to a catastrophic structural, electrical, or mechanical problem. For obvious reasons then, corrosion is a serious concern to the owners and operators of military and commercial aircraft. Aircraft encounter and endure a number of atmospheric conditions, as well as diverse operating environments and conditions within the various aircraft systems. Therefore, it is critical to know and understand the potential environments and to take these into account when selecting materials during design. If materials are selected improperly, the consequence can be extremely costly corrosion damage that can result in the non-availability of aircraft, high maintenance and repair costs, or in extreme cases the complete loss of aircraft and human life.

Traditionally aircraft (especially military aircraft) have been oriented toward high performance and efficiency, and the materials chosen during the design stage have been chosen for properties other than corrosion resistance, such as high strength-to-weight ratios. This lack of attention to corrosion resistance has become increasingly evident in the maintenance required just to keep legacy aircraft flying safely. Furthermore, as it has become more common to operate aircraft that have exceeded their intended design life, corrosion maintenance becomes more time consuming and expensive. Therefore, a number of corrosion preventative methods and strict inspection and maintenance routines are employed in order to prevent failures due to corrosion.

The complexity of an aircraft, whether it is military or commercial, often makes corrosion prevention a nearly impossible task. Proper materials selection, design for inspectability and strict maintenance procedures, however, will result in a dramatic reduction of corrosion problems and a significant cost savings in maintenance. The following section provides a brief overview of

the types of environments encountered by aircraft, some of the major components susceptible to corrosion, types of metals used, forms of corrosion, prevention and control methods, maintenance, inspection, and monitoring techniques.

5.1.1   Typical Corrosive Environments

The corrosion of metallic components on aircraft can be difficult to predict due to the dynamic environmental conditions experienced during operation. As opposed to stationary structures, aircraft structures and systems encounter many different operational environments, including changing atmospheric and internal system conditions. Aircraft fly at high speeds, requiring substantial thrust, and thus operate under extreme and rapidly changing conditions of temperature, stresses, and vibrations. Wear, fatigue and stress in combination with an aggressive environment can accelerate the rate of corrosion. Geographic location, altitude, and weather can also affect the corrosion of aircraft and their systems.

5.1.1.1   Atmospheric Environments

Whether in-flight or on the ground aircraft are constantly exposed to the atmosphere. For example, they must endure varying temperature, atmospheric contaminants (e.g. pollution), moisture, marine environments, etc. The most corrosive atmospheric environments are typically those containing a significant amount of pollution. Pollutants include corrosive agents such as sulfur dioxide, ammonia and smoke particles. Marine and tropical atmospheric environments are known to be highly corrosive as well. The intended operational atmospheric environments are important considerations when selecting materials for use on or within the aircraft.

5.1.1.2   Marine Environments

The marine environment is the most severe environment that aircraft encounter in terms of corrosion. Naval aircraft, therefore, are especially at risk, as they operate and are located near seawater environments throughout most of their operational lifetime. Aircraft on aircraft carriers are subjected to an especially corrosive environment. That is, they are exposed to a marine atmosphere and they are often subjected to salt spray, which is extremely corrosive. They are also subjected to the jet engine exhaust, which contains very corrosive gases and particles. Naval aircraft operating in tropical conditions are subjected to even higher corrosion rates due to increased temperature.

5.1.1.3   Desert and Other Environments

Desert environments can also be particularly corrosive to low flying aircraft. Because of dust in the atmosphere, this type of environment can cause erosion corrosion on the exterior leading edges of the wings and in the components surrounding air intakes.

Take-off and landing conditions must be considered as they may also impact the corrosion of aircraft. That is, during take-off and landing the aircraft may be subjected to dust, gravel, stones, and de-icing salts from the runway. Any of these may damage the paint and ultimately accelerate the rate of corrosion.

5.1.1.4   Maintenance Hazards

Metallic components on aircraft also endure harmful conditions simply from operation and maintenance. Some of the potentially corrosive hazards are listed below.[3]

- Oils and hydraulic fluids
- Cleaning materials and paint strippers
- Maintenance actions causing scratches and abrasions
- Accidental damage during maintenance and in operation
- Battery acid
- Exhaust gases
- De-icing and de-frosting fluids
- Toilet and galley spillages
- In flight turbulence causing spillage
- Cargo breakage and/or spillage
- Contaminated fuel (kerosene)

5.1.2   Major Components Susceptible to Corrosion

Some areas of the aircraft experience more severe environmental conditions than others, and thus, different areas of aircraft corrode at different rates. Moreover, certain aircraft components have chronic corrosion problems which require adherence to rigid maintenance procedures. Some of the more corrosion prone areas for different types of aircraft are listed in Table 32, but this list is far from exclusive. A few of the more notable aircraft components that are especially susceptible to corrosion are lap joints; wires, connectors and other electronic components; fasteners and fastener holes; landing gear; other structural components; and engine components.

Table 32   Corrosion Prone Areas on Different Types of Aircraft[3]

Transport Aircraft	Fighter Aircraft	Helicopters
▪ Main undercarriage ▪ Nose undercarriage ▪ Rudder and elevator shroud areas ▪ Aileron and flap track area, flap tracks and trailing edges ▪ Freight doors and ramps ▪ Access doors ▪ Control cables ▪ Leading edges, hinge lines and air ducts ▪ Radome area	▪ Missile and gun blast areas ▪ Engine intake areas ▪ Cockpit frames ▪ Wing fold areas	▪ Main rotor head assembly ▪ Tail rotor assembly ▪ Transmission housing ▪ Main rotor blades and leading edges

5.1.2.1   Aircraft Skins

Aircraft skins have a tendency to corrode after long periods of exposure to corrosive environments. The corrosion of skins, however, usually originates near fasteners, lap joints, and faying surfaces, along rivet lines or where protective coatings have been damaged or left untreated.

5.1.2.2   Joints and Fasteners

Lap joints, which have crevices, are especially prone to corrosion unless proper preventative measures are taken. Any structural detail like a joint where there is a gap between adjacent components that moisture can seep into and become trapped is highly susceptible to corrosion. Sealants and water-displacing corrosion preventative compounds are especially good at preventing corrosion in these types of components.

Fasteners and fastener holes are known to be a prime target as the source of corrosion problems. Fasteners in contact with the aircraft skin can be susceptible to galvanic corrosion if the metals are sufficiently dissimilar and do not have the proper coating. Fasteners, however, should be slightly cathodic to the material they are joining, which will further reduce the effects of galvanic corrosion. In addition to galvanic corrosion, fasteners can be susceptible to stress corrosion cracking (SCC), since they are inherently withstanding stresses or loads. It is also important to consider fastener materials that are not susceptible to hydrogen embrittlement. Joints that are critical to the structural integrity of the aircraft should use fasteners that are highly resistant to the corrosive environment that they will be operating in. Fastener holes are susceptible to corrosion fatigue and to SCC due to the concentration of stress at a point in the hole. Riveted structures are especially susceptible to exfoliation corrosion. Two methods to prevent this corrosion are to select a proper metal and to use a chromate sealant material on the fasteners.

5.1.2.3   Electrical Systems

Electrical systems that have wires, connectors and contacts are known to have problems with corrosion. Moisture or humid environments can lead to corrosion of the metal parts in these systems. A small amount of corrosion can have a significant impact on these systems by disabling them from working properly. Therefore, proper packaging and encapsulation will assist in preventing corrosion. Figure 45 shows an example of corrosion that occurred on electrical connectors for the main fuel shutoff valve on an F-16.
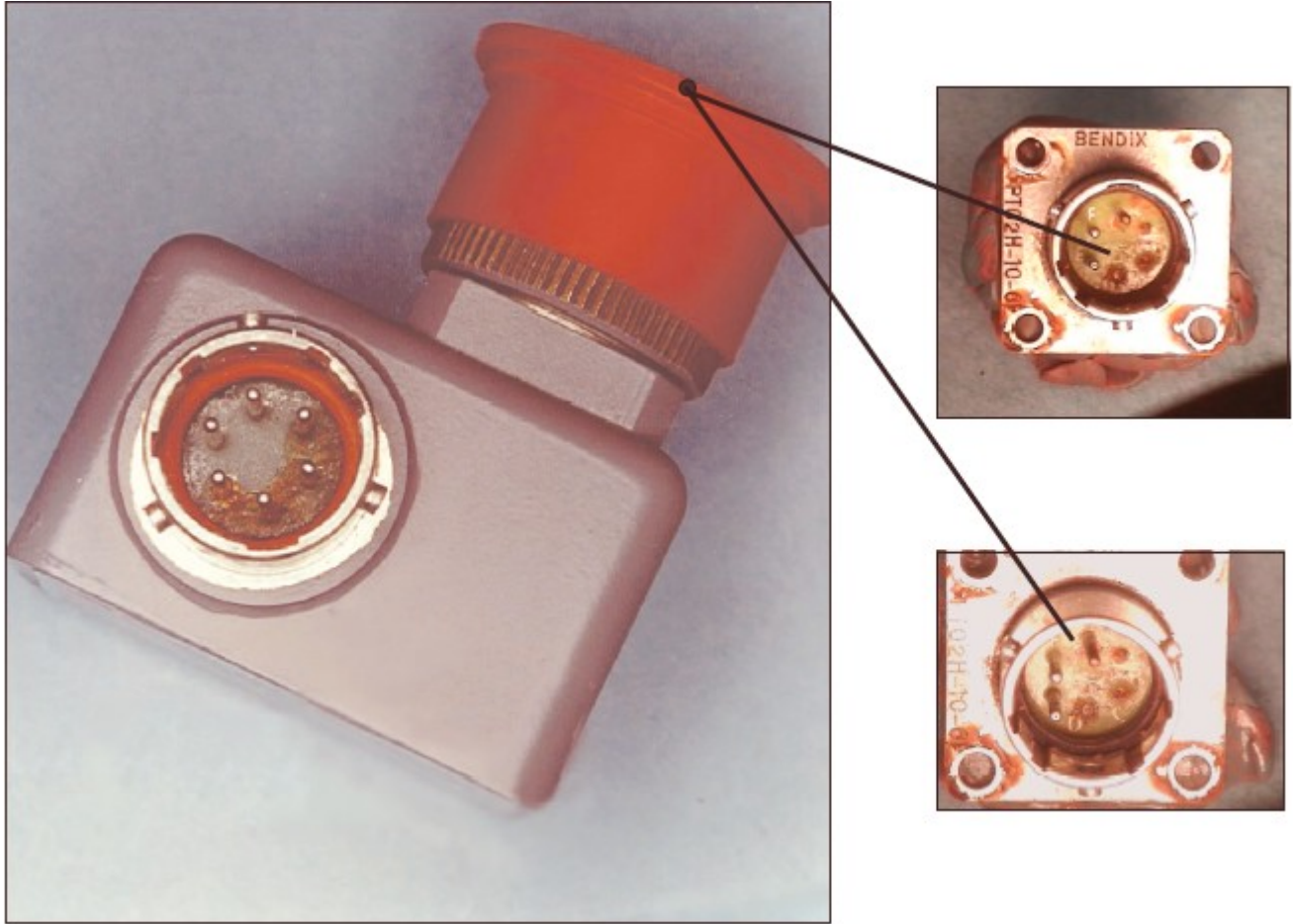
Figure 45   Corroded Connectors on Air Force F-16 Main Fuel Shutoff Valve[42]

5.1.2.4   Structural Components

Structural components that withstand stresses and are exposed to corrosive environments are susceptible to failure due to accelerated forms of corrosion such as SCC. Furthermore, joints containing sufficiently dissimilar metals will experience accelerated corrosion. Selection of materials that have a high resistance to SCC are important if they will be used to support significant loads or withstand high stresses.

5.1.2.5   Aircraft Engines

Aircraft engines house particularly corrosive environments, where high temperatures and corrosive liquids and gases are constantly present during operation. Aircraft power plant systems are known to be susceptible to corrosion, particularly hot corrosion. These systems operate in extremely high temperatures; some parts reach temperatures of approximately 2260°F.[19]   In turbine engine components, corrosion and failure can be accelerated if the components become displaced such that they rub against each other and generate an excessive amount of heat. These extremely high temperatures cause rapid oxidation of components including those made from titanium. Thus, precise design and material selection are required in order to battle the potential accelerated forms of corrosion. The engine air inlet has been known to be especially susceptible

to corrosion because of airborne solid particles and rain erosion that cause damage to the surface of the metals and coatings.

5.1.2.6   Helicopter Components

Helicopters have components that are unique and thus they have their own corrosion problems. For example, the rotor heads, main rotor blades, and tail rotor blades are all directly exposed to the atmospheric environment, and consequently may experience accelerated corrosion compared to internal components. Furthermore, the leading edges of rotor blades are susceptible to damage from airborne solid particles, such as dust and sand, as well as rain erosion. In effect, this may increase the susceptibility of these components to corrosion.

5.1.2.7   Other Systems and Areas

Bilge areas (pits or sinks in the fuselage lower structure) on aircraft where waste (hydraulic fluids, water, dirt, loose fasteners, drill chips and other debris) is collected are very susceptible to corrosion. This is because the waste accumulates due to leaks, spillage, etc. and forms the right conditions for general corrosion or SCC to occur, especially when the area cannot be periodically inspected and cleaned.

Other areas, systems and components in aircraft are prone to corrosion. These include exposed hardware, such as control surface actuating rods and fittings, which may corrode due to coupling with dissimilar metals or damaged or deteriorated protective coatings. Another area is the undercarriage bay, where wheel wells for example are susceptible to damage from runway debris. Battery compartments and vent openings are susceptible to severe corrosion from battery spillage. Fuel tanks are susceptible to corrosion due to the ingress of moisture originating from the fuel itself. Areas in the path of engine exhaust (exhaust trail areas) are very susceptible to corrosion due to the corrosive nature of exhaust gases.

Table 33 provides a listing of aircraft components, the type of metal used to construct them, and the forms of corrosion that have been observed. This is just a sampling intended to convey the vast nature of the corrosion problems observed on aircraft. Many solutions have since been applied in order to prevent corrosion in these areas from recurring.

Table 33   List of Aircraft Components and Examples of Observed Forms of Corrosion[19]

Aircraft Component	Type of Metal	Form of Corrosion
Fasteners	Cadmium-plated steel (in contact with aluminum)	Galvanic
Skin	Aluminum alloy (in contact with electrically conducting adhesive)	Galvanic
Kingpin Lug	7075-T6 aluminum alloy (in contact with steel bushings)	Galvanic
Flap Control Lever Arm	Magnesium alloy casting with zinc-chromate primer and epoxy topcoat (in contact with steel balls)	Galvanic
Stringer	Aluminum alloy with chromate pretreatment and primer	Uniform
Helicopter Skin	Magnesium alloy with chromate conversion coating	Uniform
Honeycomb Structure	Aluminum	Uniform
Fasteners	Steel	Uniform
Helicopter Structural Cleat	Magnesium alloy casting with chromate and sealant	Pitting
Stringer End Cap	Magnesium alloy with chromate and primer	Pitting
Spring Wire	High carbon steel	Pitting
Hydraulic Cylinders	2024-T4 aluminum alloy	Pitting
Brake Lining Carrier	Pure beryllium	Pitting
Tip Tank Latch Knob	4340 steel	Pitting
Wing Flap Hinge Bearings	Chromium-plated 440C stainless steel	Pitting
Panel Joint	Magnesium	Crevice
Skin Joint	Magnesium alloy	Crevice
Helicopter Spindle Sleeve	Martensitic steel	SCC
Large Bolts	High-strength steel	SCC
Helicopter Landing Gear Drag Strut	300M steel	SCC
Landing Gear Locking Cylinder	7079-T6 aluminum alloy	SCC
Landing Gear H-Link Structure	7079-T6 aluminum alloy	SCC
Spars on a Vertical Fin	7079-T6 aluminum alloy with surface treatment	SCC
Vertical Stabilizer Bearing Housing	7079-T6 aluminum alloy	SCC
Landing Gear Bogie	7075-T6 aluminum alloy	SCC
Hydraulic Cylinders	7075-T6 aluminum alloy	SCC
Nose Landing Gear (Fork and Strut)	7075-T6 aluminum alloy	SCC
Fastener Holes	Aluminum alloy	SCC
Landing Gear Forging	Aluminum-copper alloy	SCC
Landing Gear Retraction Cylinders	4340 steel	SCC
Stabilizer Bracket	Aluminum alloy	Exfoliation
Wing Box Lower Panel and Fastener Holes	7075-T6 aluminum alloy	Intergranular
Leading Edge of Rotor Blade	2024 aluminum alloy	Intergranular

Table 33, continued - List of Aircraft Components, Examples of Observed Forms of Corrosion

Aircraft Component	Type of Metal	Form of Corrosion
Leading Edge of Rotor Blade	2024 aluminum alloy	Exfoliation
Fuselage Skin	Aluminum alloy	Filiform
Pylon Tank	6061-T6 aluminum alloy	Filiform
Ailerons	2024 aluminum alloy	Filiform
Flaps	2024 aluminum alloy	Filiform
Propeller Shaft Ball Bearings	AISI E51100 steel	Fretting
Lower Boom of Wing Forward Spar	2014 aluminum alloy	Fretting
Hinge Pin	4340 steel with cadmium-plating	Corrosion Fatigue
Landing Gear Wheel	QE22A magnesium alloy	Corrosion Fatigue
Rivets	5052 aluminum alloy	Corrosion Fatigue
Integral Fuel Tank	2024 aluminum alloy	Microbiological
Landing Gear Cylinders	4340 steel	Hydrogen Embrittlement
Propeller Retaining Bolt	Steel with cadmium coating	Hydrogen Embrittlement
Nose Gear Strut	Steel	Hydrogen Embrittlement
Flap Control Return Spring	Carbon steel with cadmium plating	Hydrogen Embrittlement
Landing Gear Pivot Pins	4340 steel with chromium plating	Hydrogen Embrittlement
Landing Gear Drag Link Bolt	4340 steel with cadmium-plating	Hydrogen Embrittlement
Turbine Engine Compressor Disks	Ti-7Al-4Mo	Hot-Salt SCC
Low-Pressure Compressor Casing	Magnesium alloy EZ33	Fretting
Compressor Blades	AM-355 stainless steel	Pitting
Thrust Reverser Doors	422 stainless steel with MoS_2 film	Pitting
Airframe Attachment Bolt	PH13-8Mo steel	SCC
Ejection Seat Swivel	7075-T651 aluminum alloy	SCC
Aircraft Wing Bracket	7178-T6	Exfoliation
Aircraft Controller Diaphragm	17-7PH stainless steel	SCC
Fuel Line Tubes	6061-T6 aluminum alloy	Intergranular
Wing Panel	7075-T6 aluminum alloy	Uniform
Wing Spar	7079-T6 aluminum alloy	SCC
Pitostatic System Connectors	2024-T351 aluminum alloy	SCC
Pylon Strut	7075-T6 aluminum alloy	SCC
Wing Leading Edge	AZ31B magnesium alloy	Corrosion Fatigue

5.1.3   Forms of Corrosion Observed

SCC, corrosion fatigue and hydrogen embrittlement are some of the most serious forms of corrosion on aircraft because they can result in fractures and ultimately catastrophic failures. Other forms of corrosion can be just as serious, if gone unnoticed or untreated. .

5.1.3.1   Uniform Corrosion

Uniform corrosion on aircraft is the easiest form to notice and least dangerous, unless it is left untreated. It is often the result of a breach in the protective coating, where the coating was damaged, improperly applied, or deteriorated over time.

5.1.3.2   Crevice Corrosion

One of the most common forms of corrosion observed to occur on aircraft is crevice corrosion. This occurs when liquid becomes trapped in small gaps between adjacent components or within a single part. Therefore, proper protective coating, sealing or drainage of components is critical to preventing this form of corrosion.

5.1.3.3   Galvanic Corrosion

Special attention and preparation must be paid to components that have two dissimilar metals in contact with each other; otherwise, galvanic corrosion may occur. Galvanic corrosion in aircraft is common between steel and aluminum, titanium and aluminum, or titanium and steel. A common place to find galvanic corrosion is between a fastener and the adjacent metal. If they are dissimilar, it is better to have the fasteners constructed from a metal that is slightly more cathodic than the adjacent metal.

Most importantly, however, galvanic corrosion can be easily avoided by not allowing two dissimilar metals to come into contact. If it is necessary to have two dissimilar metals in contact, then the two metals should be chosen to minimize their galvanic couple or electrical potential differences. Moreover, finishing and sealing methods or other guidelines are usually used to properly prevent components from galvanic corrosion.

5.1.3.4   Pitting Corrosion

Pitting corrosion is more frequently observed on aircraft that serve in marine environments due to the concentration of chloride ions in such environments. Pitting corrosion often occurs when the protective coating is damaged resulting in an area that is susceptible to a concentrated attack. This can happen during manufacturing or maintenance of the aircraft, or the protective coating can wear down over time. Pitting also has a tendency to occur if the metal has a concentration of impurities that are more susceptible to corrosion than the base metal or alloy. Moreover, surface deposits of sediment, dirt, or grease during flight, maintenance or storage can also lead to pitting corrosion.

5.1.3.5   Stress Corrosion Cracking

SCC is one of the more common failures observed in the structural components of aircraft. This form of corrosion can be difficult to discover since it does not necessarily occur at the surface.

Since many aircraft components are subjected to high stresses, SCC is a significant concern. Proper design, material selection, and application of protective coatings and surface treatment are key to protecting against SCC in aircraft components. Any joint or other component that must endure significant stress may be susceptible to SCC.

5.1.3.6 Filiform Corrosion

Filiform corrosion often occurs between the surface of the metal and protective layers applied over it. It has been observed on fuselage skins, near fastener holes, wing skins, pylon tanks, stabilizers, and trailing edge flaps as well as other aircraft components. Since filiform corrosion occurs under the surface of a coating, it can go undetected for a long time. Once filiform corrosion has been identified on an aircraft component, it may be possible to remedy it. That is, corrosion products can often be removed and a new protective coating be applied. Furthermore, CPCs are used to prevent filiform corrosion.

5.1.3.7 Fretting Corrosion

Fretting corrosion occurs in aircraft systems having surfaces that move relative to another surface. This can occur with structural components since high frequency vibrations are common in aircraft. It usually acts in conjunction with wear and in the presence of oxygen. Fretting corrosion has been observed in many aircraft components including hinge pin bearings on ailerons, elevators, rudders, and flap structures, control pulley bearings, universal joint bearings, propeller and propeller control bearings, housings, and shafts, instrument bearings, spline connections, pin joints, clamps, and riveted lap joints.[19] Fretting damage on flying control hinge pins for aircraft is shown in Figure 46.
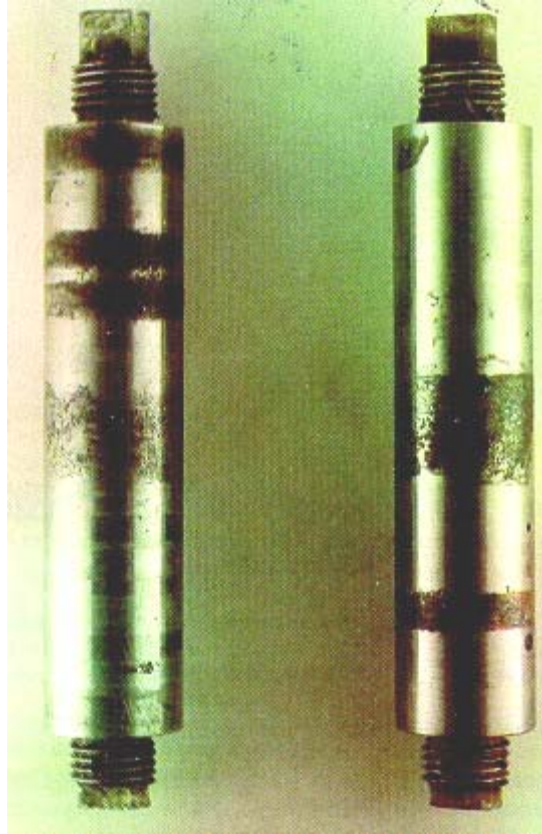
Figure 46   Fretting Damage in Two Flying Control Hinge Pins[3]

To reduce the risk of fretting corrosion friction can be either eliminated or increased to the point of having zero slip between adjacent surfaces. Lubrication is commonly used to reduce friction and increased pressure is used to reduce the amount of slip between surfaces.

5.1.3.8   Corrosion Fatigue

Corrosion fatigue in aircraft occurs as a result of the combination of fatigue from high cyclic stresses and corrosive environments, to which aircraft are exposed. Short of component failure, corrosion reduces the fatigue strength of the component. Corrosion fatigue has been observed around aircraft fastener holes and on helicopter rotor assemblies, landing gear wheels[3], and rivets.

5.1.3.9   Microbiological Corrosion

Microbiological corrosion has been known to occur in integral fuel tanks on aircraft, where the microbes would feed on kerosene fuels and condensed water vapor, or sometimes synthetic rubber. Fungi is usually the culprit in microbiological corrosion of aircraft, but bacteria and yeast have also initiated damage. Of course tropical climates are commonly associated with breeding microbes. Polyurethane coatings are penetrable by microbes; therefore, biocides are incorporated into the coating material itself. Good fuel quality is important to prevent microbiological corrosion.

5.1.3.10   Hydrogen Embrittlement

Aircraft components made of steel are especially susceptible to hydrogen embrittlement. The hydrogen is usually introduced into the material sometime during the plating processes when the component is being manufactured. Steel parts in landing gear have been observed to fail due to hydrogen embrittlement. Steel bolts and fasteners, nose gear struts, the flap control return spring, main landing gear pivot pins, and the main landing gear drag link bolt have also had problems with hydrogen embrittlement.[19]

5.1.3.11   Erosion Corrosion

Erosion corrosion occurs on aircraft when a fluid continuously flows against a metal surface resulting in a gradual deterioration of the metal. Erosion corrosion can be accelerated if the fluid is flowing at a high velocity, and/or if it is carrying abrasive particles. Therefore, aircraft flying through desert/sand environments with airborne sand particles are susceptible to erosion corrosion on the exterior of the aircraft. Damage from erosion corrosion on the undercarriage of a transport aircraft is shown in Figure 47
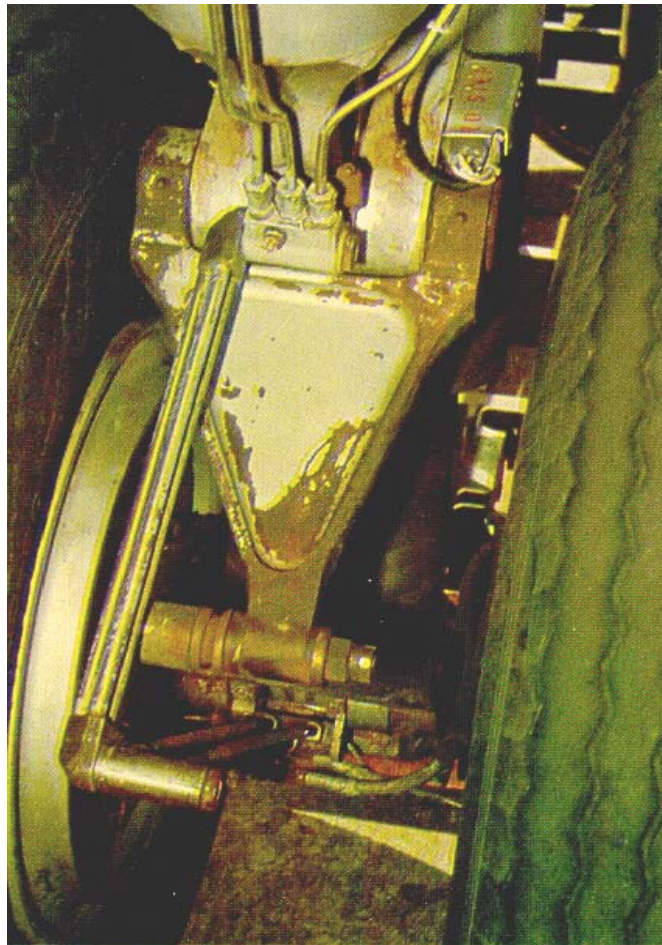
Figure 47   Erosion Corrosion Damage on the Undercarriage of a Transport Aircraft[3]

5.1.3.12   High Temperature / Hot Corrosion

High temperature and hot corrosion have a tendency to occur in or near the engine components of aircraft, since they reach very high temperatures. A very damaging form of high temperature corrosion has been known to occur in engine components made from titanium. This occurs when the titanium oxidizes so rapidly that it causes combustion. Hot-Salt SCC occurs in aircraft components that are exposed to high stresses, high temperatures and marine environments.

5.1.4   Types of Metals used in Aircraft

Due to their low density, relatively low cost, and many other desirable properties, corrosion resistant aluminum alloys are the primary construction materials for aircraft. Titanium alloys, special grade steels, nickel alloys, and magnesium alloys are some of the other metals used to construct certain aircraft components.

5.1.4.1   Aluminum Alloys

Aluminum alloys are the most common materials used for the construction of aircraft systems and components. They have been used for the wing and fuselage skins, spars, cowls, fasteners, electrical housings, hydraulic tubing, as well as a number of other components.

Cast aluminum alloys are used less in aircraft systems than the wrought form, but they have been used for impellers, pump and compressor components, and aircraft wheels as well as other aircraft components. They are generally very resistant to corrosion, especially SCC and offer good weldability.

Wrought aluminum alloys are extensively used in aircraft. Among these some of the most important alloys for aircraft are the 2000- and 7000-series. The heat treatment used to process the material can make it sensitive or resistant to corrosion. In particular, the T6 temper of 7075 and 7079 alloys have been observed to be susceptible to SCC in airframe structures. Precipitation hardened 7000-series alloys are more resistant to general corrosion than the 2000-series alloys, but they are still especially susceptible to SCC as well as exfoliation if they are not specially heat treated to counter these forms of attack. T-73 and T-76 tempers are therefore recommended for 7000-series aluminum alloys so they can resist SCC and exfoliation, while minimizing the loss in strength compared to the T6 condition. Of the 2000-series aluminum alloys, 2024 is acceptable to use where SCC could be a problem. The 6000-series aluminum alloys generally offer better corrosion resistance compared to the 2000- and 7000-series of alloys. 6000-series alloys that have been precipitation hardened, in general, exhibit little change in corrosion resistance. Copper containing aluminum alloys, such as 6061 are slightly less resistant to corrosion.[3]

Non-heat treatable, wrought aluminum alloys are also used for aircraft applications. The 5000-series alloys with alloying additions of less than 3% exhibit excellent resistance to corrosion. Alloys having higher alloy contents are much more susceptible to exfoliation and SCC. However, 5090 aluminum, which contains up to 7% magnesium, exhibits excellent resistance to SCC and exfoliation, and in some cases may be used instead of 7075-T6.[3]

5.1.4.2   Steels

Carbon and low alloy steels are typically only used in aircraft when the mechanical property requirements are most important. These steels generally show poor corrosion resistance and are typically susceptible to uniform corrosion, pitting and intergranular attack. Small adjustments in the composition of carbon steels may lead to improved corrosion resistance, although it may also result in higher susceptibility to SCC in certain environments.

Ultrahigh strength steels have been used in gears, landing gear components, pinions, connecting rods, and bolts in aircraft. This type of steel, however, is very susceptible to corrosion, and special compositions and treatments along with a form of corrosion protection should be used to provide the necessary corrosion resistance.

Austenitic and martensitic stainless steels have been used primarily in aircraft engine systems, but may have other less significant applications to aircraft as well. The austenitic stainless steels have better corrosion resistance in general compared to the other types of steels. They may, however, be especially susceptible to SCC and intergranular corrosion or pitting and crevice corrosion under more severe conditions. Martensitic stainless steels also have greater corrosion resistance in general compared to other types of steels, but not quite as good as the austenitic stainless steels. These steels are especially susceptible to SCC and hydrogen embrittlement.

Age hardening steels have been used for high strength fasteners, thin section parts and aircraft pressure vessels. Age hardening steels typically have a fair resistance to corrosion in general, but are especially susceptible to crevice corrosion, pitting and SCC. Nickel chromium steels have been used for turbine discs and exhaust components in aircraft. They exhibit good corrosion and oxidation resistance, and are especially useful in high temperature oxidizing atmospheres such as those in engine environments.

Some typical alloys used in aircraft and some corrosion problems that have been observed as well as solutions employed are presented in Table 34.

5.1.5   Corrosion Prevention and Control – Methods and Maintenance

Proper material selection during the design stage, and proper application of coatings and finishing is good practice in preventing corrosion in aircraft. Furthermore, in order to keep aircraft in safe operation they must be maintained with great care. MIL-HDBK-1568 is an active standard intended to be used for setting up sound material selection practices and finishing treatments throughout the design, development, production and operational stages of aircraft systems.[43]   The handbook determines some of the requirements for materials, processes and techniques and it identifies the necessary steps for setting up an effective corrosion prevention and control program. Following the steps outlined in this standard will help minimize life-cycle cost impacts due to corrosion and also improve the reliability of aircraft systems.

5.1.5.1   Material Selection and Processing

Materials for aircraft are predominantly selected for their performance value, rather than for their corrosion resistance. For many reasons, however, corrosion resistance is a critical aspect to be considered when selecting materials for aircraft. Resistance to stress corrosion cracking in the intended aircraft operating environments, for example, is an extremely important attribute when selecting an alloy for a structural applications on the aircraft. Another example of an aspect of

material selection that can lead to preventing a corrosion problem is not selecting materials that absorb moisture.

Table 34   Aircraft Alloys with Associated Problems and Solutions[6]

Alloy	Problems	Solutions

Aluminum
    Wrought 2000 and
    7000 series sheets,
    extrusions, forgings
 	
Cast,
    Al-Si-(Mg-Cu)
	Galvanic corrosion
	Pitting
	Intergranular corrosion
	Exfoliation
	Stress corrosion cracking
	
	Usually corrosion resistant
		Cladding
		Anodizing
		Conversion coatings
		Ion vapor deposited Al
		Painting

Low-alloy steels
    4000 and 8000 series,
    300M fasteners.
	Uniform corrosion
	Pitting
	Stress corrosion cracking
	Hydrogen embrittlement
		Cadmium plating
		Phosphating
		Ion vapor deposited Al
		Painting

Stainless steels
    300 series austenitic
 	
    400 series martensitic
    and precipitation
    hardening (PH) series
	Intergranular corrosion
	Pitting
	Pitting
	Stress corrosion cracking
	Hydrogen embrittlement
		Alloy Selection
		Annealing
		Heat Treatment
		Shot Peening
		Corrosion Inhibitors

Magnesium alloys	Uniform corrosion Pitting Stress corrosion cracking	Anodizing Conversion coatings Painting

5.1.5.2   Design

There are also many ways to prevent corrosion through design. All aircraft components should be designed with proper drainage so they won't collect moisture or liquid. This is critically important because trapped moisture can quickly lead to corrosion. CPCs, which are typically hydrophobic, are applied to faying surfaces (a surface in contact with other surface) and other areas to seal components from water.

5.1.5.3   Cladding

Many aluminum alloys used on aircraft, especially for wings and skins, are clad with an alloy (usually aluminum, e.g. AA 7072) that is more anodic compared to the base alloy. This improves corrosion resistance by providing cathodic protection. The cladding will preferentially corrode, and when the corrosive attack reaches the base aluminum alloy the corrosion will then proceed laterally rather than perforating the base. This cladding method therefore provides valuable protection of thin aircraft components, such as fuselage skins, that might otherwise be easily perforated by corrosive attack.[3]

5.1.5.4   Coatings

The use of protective coatings is an effective way to prevent corrosion, and is commonplace. Sealants are used to seal fay surfaces to prevent crevice corrosion in joints. Examples of areas on the aircraft that typically use sealants include: skin-to-stringer, skin-to-shear tie joints, longitudinal and circumferential skin splices, skin doublers, spar web-to-chord and chord-to-skin joints of the wing and empennage, wheel well structure, pressure bulkheads, and some fasteners.[44] Priming metal parts that will be in contact with other types of metals is very important to protect against galvanic corrosion. The primers used should be resistant to hydraulic fluids. Thin, inorganic coatings are typically used for corrosion protection of components that require close tolerances. The minimum requirements to be considered for finishes, protective coatings, and sealants used in the protection of aircraft and aerospace weapons systems is given in MIL-STD-7179 (active).

Corrosion preventive compounds (CPCs) are commonly used to protect aircraft components from corroding, and they are often applied after most maintenance procedures for temporary protection of the aircraft from corrosion. Water-displacing CPCs are used to seal cracks and crevices to prevent moisture penetration thereby greatly reducing the risk of corrosion.

5.1.5.5   Inhibitors

Inhibitors are used on aircraft either to reduce the rate of a corrosion reaction that has already been initiated on a metallic surface, or to protect the surface by interacting with the environment to reduce the potential for corrosion. Types of inhibitors used in aircraft applications include passivating inhibitors, organic inhibitors, and vapor phase inhibitors (volatile corrosion inhibitors). Passivators are commonly used on aircraft, since they are very effective in decreasing the rate of corrosion by making the metal more noble.

Inhibitors can be and often are included in the formulation of surface coatings, primers, paints, sealants, greases or jointing compounds. They can also be added to cleaning mixtures used to wash the surface of the aircraft so that they are strategically deposited on the surface over a wide area to augment its resistance to corrosion.

5.1.5.6   Grease

Some CPCs are available as greases which serve the dual purpose of lubrication and corrosion protection. Other greases contain inhibitors to provide additional resistance to corrosion. Whenever possible, greases with corrosion prevention capability should be used on aircraft.

5.1.5.7   Maintenance

A strict corrosion control and prevention maintenance program has been instituted by the military. To minimize corrosion, every aircraft must be maintained diligently. Some recurring maintenance practices include washing, repainting, paint renewal, corrosion inhibition, and the application of CPCs.

It is important to have access to all parts of the aircraft, so that it can be inspected and maintained properly. Regular inspection and maintenance are clearly the best method to prevent or stop corrosion from causing critical damage to the aircraft. This in turn will reduce the maintenance required due to corrosion damage.

5.1.6   Corrosion Monitoring

While the external aircraft skin is easier to inspect for corrosion, other parts of the aircraft are far more difficult to examine. Inspection and monitoring of aircraft, therefore, can be expensive.

Sensors embedded in future aircraft components may be used for self monitoring and early warning of corrosion, coating degradation and fatigue damage. This would allow for expedited maintenance and prevention of catastrophic damage due to corrosion, thus reducing cost of maintenance and aircraft downtime.

5.2   Ships and Submarines

Ships, submarines and other watercraft are invariably forced to operate in one of the more severe, natural environments in terms of corrosion. The entire life of a watercraft may be spent partially or completely submerged in and exposed to seawater, and thus, corrosion is a major issue that must be accounted for. Consequently, design, material selection, and maintenance are all critical aspects in safely and cost effectively maintaining an active ship or submarine. Otherwise, the labor intensive and costly procedures of repair and replacement will be required. This section describes the typical corrosive environments encountered by ships and submarines, specific components that are especially susceptible to corrosion in these environments, types of metals commonly used, forms of corrosion typically observed, and common corrosion prevention and control methods. Even though this section focuses on surface ships and submarines, much of the information may be applicable for any application or system operating in a marine environment.

5.2.1   Typical Corrosive Environments

Seawater, sea aerosols, rain, dew, condensation, and high humidity are the main contributing factors to corrosion in marine environments.[45] Fundamentally speaking, moisture is the primary cause for corrosion, and seawater is the most corrosive natural medium faced by watercraft. More specifically, seawater, in terms of corrosion, is one of the most severe environments due to the high concentration of chloride ions in combination with the high moisture content and oxygen present in the air and seawater. In general, the rate of corrosion is accelerated by the presence of chloride ions, which, together with the moisture, is mostly why marine environments are so severe. The major constituents of seawater are given in Table 35. The corrosivity of seawater is largely dependent on:

- Chloride content
- pH

- Oxygen content
- Temperature

Table 35   The Major Constituents of Seawater (Chlorinity = 19.00 Parts Per Thousand)[46, 47]

Anion	Parts Per Million	Equivalents per Million*	Parts per Million per Unit Chlorinity**
Chloride, Cl^-	18,980.0	535.3	998.90
Sulfate, SO_4^{2-}	2,649.0	55.1	139.40
Bicarbonate, HCO_3^-	139.7	2.3	7.35
Bromine, Br^-	64.6	0.8	3.40
Fluoride, F^-	1.3	0.1	0.07
Boric acid, H_3BO_3	26.0	-	1.37
Total		593.6	
Cation	Parts Per Million	Equivalents per Million*	Parts per Million per Unit Chlorinity
Sodium, Na^+	10,556.1	159.0	555.60
Magnesium, Mg^{2+}	1,272.0	104.6	66.95
Calcium, Ca^{2+}	400.1	20.0	21.06
Potassium, K^+	380.0	9.7	20.00
Strontium, Sr^{2+}	13.3	0.3	0.70
Total		593.6	

*Equivalents per million is the concentration (parts per million) divided by the equivalent atomic weight
**Parts per million per unit chlorinity is the parts per million divided by 19 parts per thousand (chlorinity = 19 parts per thousand)

5.2.1.1   Geographic Location

The severity of the marine environment can vary significantly depending on a watercraft's geographic location and climate. Tropical marine climates are far more corrosive, for example, than cold marine climates, because usage temperature has a substantial impact on corrosion rate. An example of the dependence of corrosion rate on atmospheric salinity is provided in Figure 48. The figure shows the rate of corrosion in grams per square decimeter per month (y-axis) is directly dependent on the deposition rate of salt on the steel in units of mg of salt per square meter per day (x-axis).
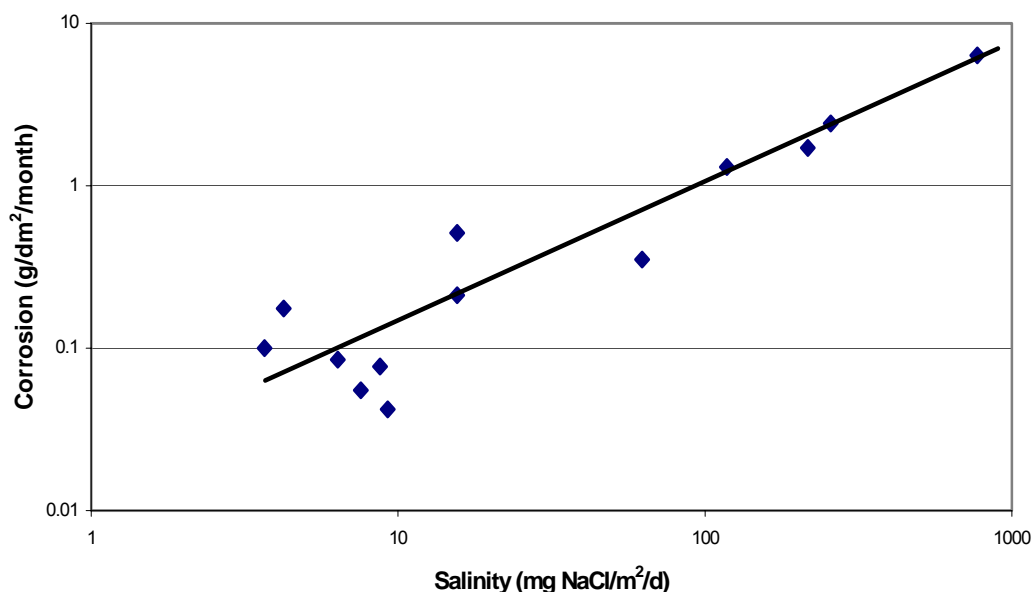
Figure 48   Corrosion of Steel as a Function of Atmospheric Salinity[48, 49]

5.2.1.2   Marine Corrosion Zones

The corrosion rate of an exterior component exposed to the marine environment is somewhat dependent on whether it is above the seawater, in the tidal zone or completely immersed in the seawater. The concentration of chlorides originating from seawater is dependent on the proximity to the sea and decreases with distance and altitude. The reason for the lower corrosivity at higher altitudes above the water is because there is less precipitated salt spray to act as the electrolyte, and also because of higher temperature and lower humidity. Waves represent another potentially damaging aspect of the marine environment, since they promote further corrosive attack on surface ships. Different bodies of water have different sized waves. Of course, the larger the wave, the more corrosive potential it has. The splash zone is most destructive in terms of corrosion, since the seawater carried by waves slaps against the ship resulting in an erosion effect combined with corrosion. Salt-water spray has a similar effect. Figure 49 illustrates the effect the different zones (i.e. atmosphere, splash, tidal, and immersed) have on the corrosion rate. Clearly, the splash zone is the most corrosive.
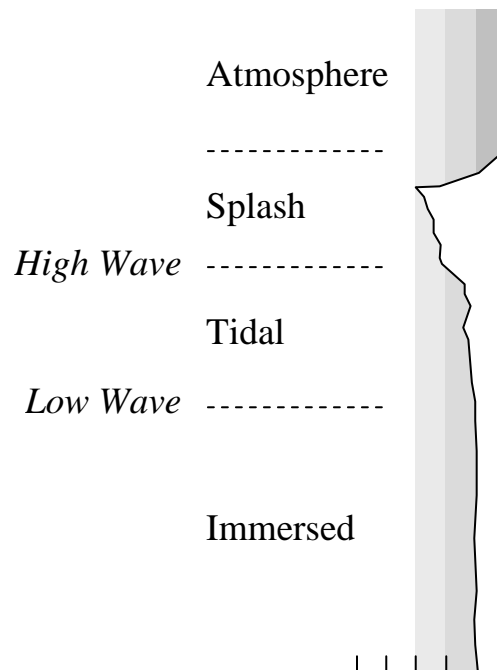
Figure 49   Corrosion Rate Profile of a Component Exposed to the Various Zones of the Marine Environment[50]

5.2.1.3   Bio-Fouling

Another influencing aspect of geographic location on corrosion is the amount of bio-fouling that can occur. Bio-fouling can cause a significant amount of corrosion on the exterior of the watercraft, but the amount of bio-fouling varies from location to location.

5.2.1.4   Shipboard Location

Furthermore, particular watercraft components may exhibit significantly varying degrees of corrosion, depending on the location of the particular piece of equipment aboard the watercraft. Any material surface onboard that is exposed to the air is likely to be exposed to the corrosive marine environment. Naturally, the exterior of watercraft as well as the topside of surface ships face the marine environment constantly and without reprieve. Salt accumulates on all surfaces, as it is always present in the marine atmosphere.

Internal systems are also susceptible to the corrosive marine environment. There is a high concentration of salt in the air, which is present in all interior locations onboard that are not sealed-off from the outside environment. Furthermore, ships and submarines have piping systems, pumps and valves that send seawater throughout the ship, while heat exchangers and condensers may also use seawater. Ballast tanks hold seawater to maintain the ship's stability in the water. Clearly, the marine environment affects more than just the exterior of the watercraft. Moreover, certain areas of the watercraft are susceptible to high temperature corrosion, such as in and near the engines which operate at high temperatures. High temperatures combined with the marine atmosphere creates one of the most severely corrosive environments.

5.2.1.5   Pollution

Polluted seawater can also pose an amplified threat of corrosion to the ship's or submarines metal structures, since it may cause corrosion to occur when it would not under normal seawater conditions. Moreover, watercraft are not necessarily safer from corrosion when they are docked in a port. This is because they may be exposed to other types of environments in addition to the sea, such as a polluted atmosphere containing acid sulfates, nitrates, and sulfur dioxides.[45] While in port the watercraft may be exposed to stagnant, brackish water that is contaminated with H_2S. Furthermore, the ships engine exhaust may pollute the environment immediately surrounding the watercraft, leading to a slightly more corrosive environment.

5.2.1.6   Velocity-Enhanced Corrosion

All watercraft that move through seawater, in some capacity, experience the corrosive effects of seawater moving over metal surfaces at some velocity. This can accelerate the corrosion rate and cause erosion corrosion. If a metal that produces a passive film in the presence of a corrosive environment is used in applications where it is in contact with high velocity seawater, the corrosion protective film may be worn away, thus exposing the metal. Some components on surface ships must also contend with salt-water sprays as the ship cuts through the water or during severe weather.

The flow of seawater over a metal component can have a marked effect on the corrosion of a metal. Some of the factors that influence the corrosion performance of a metal in flowing seawater include film forming characteristics, environment (velocity, silt, temperature, etc.), application, and the design of the component.[11] See Section 4.7 on erosion corrosion.

5.2.2   Major Components Susceptible to Corrosion

Some of the major areas of surface ships that are most susceptible to corrosion are listed in Table
36. Some of the major areas of submarines that are susceptible to corrosion are listed in Table
37.

Table 36   List of Areas on Ships Susceptible to Corrosion[45]

Topside	Interior Humid Areas
Pipe Hangers	Equipment Foundations
Electrical Connection Boxes	Pipe Hangers
Lockers	Decks/Bulkheads
Stanchions	Bilges
Boat Davits	Heads, Showers, Laundry Areas
Steam, Air, JP-5, CHT Valves	Galley, Scullery
Hawse and Chain Pipe Covers	Pump Rooms
Lights	
Foundations	
Aircraft Tiedowns	
Catapults	
Gas Turbine Generator Intake Rooms	
Electrical Stuffing Tubes	
Safety Nets	
Fueling at-sea Stations	
Well Deck Areas	
Ventilation Ducting	

Table 37   List of Some Areas and Components of Submarines that are Prone to Corrosion

Hull	Tank bulkhead
Internal tanks	Fasteners
Shaft bearing stave	Steel hull insert
Propulsion shaft	Transducer element head
Pipes	Fittings
Heat exchangers	Guide cylinders
Valves	Pumps
Periscope barrel	Bilge drain line
Sonar dome	Hydrophone mount
Free-flood spaces	

5.2.2.1   Joining

Joining of structural elements is a major part of shipbuilding, and fastener materials are usually
chosen primarily based on the strength requirements, while corrosion resistance is secondary.
Therefore, shipboard fasteners are commonly susceptible to galvanic corrosion, pitting, and
stress corrosion cracking. Table 38 provides a list of fastener materials used to join specific
types of metals that generally meet strength requirements, but also provide some corrosion
resistance.

Table 38   Fastener Materials for Joining Metals[45]

Metals Being Jointed	Fastener Material to be Used (Descending Order of Preference)
Steel with Steel	- Steel with Ceramic Coating 316 Stainless Alloy 304 Stainless Alloy - Other 18-8 Stainless Nickel-Copper (Monel)
Steel with Aluminum	316 Stainless Alloy 304 Stainless Alloy - Other 18-8 Stainless
Aluminum Alloys with Aluminum	316 Stainless Alloy 304 Stainless Alloy - Other 18-8 Stainless
Nickel-Copper with Steel or with Nickel-Copper	Nickel-Copper

5.2.2.2   Electrical Connectors

Electrical connectors are susceptible to corrosion, for example, multipin or cannon-plug connectors on shipboard electronic equipment such as interior communications or radio handsets, fire-control devices, and other electrical, radar, or radio components.[45] Heat-shrinkable tubing, vinyl tape and putty, or sealant with vinyl tape can be used to protect electrical connectors from corrosion.

5.2.2.3   Propellers

Ship and submarine propellers without proper material selection during design are susceptible to several forms of corrosion. Their rotational motion creates the potential for erosion corrosion as well as a type of galvanic corrosion. This latter form is caused by a velocity gradient of the seawater moving over the blades as they spin. The inner part of the blade has a lower rotational velocity (lower seawater velocity), while the outer part of the blade has a higher rotational velocity. This difference results in a difference in corrosion rate. Therefore, if the propeller has a protective film, it will wear/corrode away at different rates, ultimately resulting in a possible difference in electrical potential between the inner and outer part of the blade. This, then, is the cause of galvanic action, which will accelerate the rate of corrosion on the outer part of the blade. It usually is, however, not very significant in terms of the amount of corrosion.

5.2.2.4   Hull

The exterior of the ship and submarine hulls are constantly exposed to the corrosive seawater environment. Aside from uniform corrosion, it may also experience pitting, galvanic corrosion and other forms. Pitting often occurs when the hull is exposed to stagnant or slow moving seawater, such as when the vessel is in port. Galvanic corrosion is caused by an electrical coupling to a more noble material (in seawater) such as the propeller, which is typically made out of a bronze alloy. Furthermore, corrosion may occur in areas where stray electrical currents picked up from another component exit the hull and move into the electrolyte (seawater). Improperly grounded DC welding equipment is the most common cause of corrosion from stray currents.

Obviously, the hull is a critical component to a ship or submarine, and therefore, extensive protection methods must be employed. These often include protective coatings and cathodic protection.

5.2.2.5   Propulsion Shaft Sleeve

The propulsion shaft sleeve on submarines has shown to be susceptible to pitting and crevice corrosion. More recently the Monel material used for this component has been replaced with 70/30 copper-nickel and Inconel 625, which have improved the corrosion resistance.[11]

5.2.3   Forms of Corrosion Observed

Pitting, crevice corrosion and stress corrosion cracking are common forms of corrosion found on systems that operate in seawater or saltwater environments. A brief description of these forms as well as several other forms of corrosion as they pertain to ship applications is given in the following sections.

5.2.3.1   Uniform Corrosion

Marine environments are expected to cause some amount of corrosion on metal surfaces exposed for extended periods of time. Uniform or general corrosion usually occurs in stagnant or low-flow seawater at a rate of approximately 5 – 10 mils per year on mild and low-alloy steels.[11] Uniform corrosion on these types of steels is the most common form of corrosive attack on ships and submarines.

5.2.3.2   Crevice Corrosion

Crevice corrosion is a particular problem in marine environments because trapped seawater can be very corrosive and can cause serious problems rather quickly. For example, 304 stainless steel has exhibited crevice corrosion and after only a few months it penetrated through a ¼ inch thick component. This type of rapid failure is dangerous since it may jeopardize the integrity of the ship or submarine structure. For obvious reasons, crevice corrosion has a tendency to occur in components where gaskets, washers, o-rings, fasteners and lap joints are used.

5.2.3.3   Galvanic Corrosion

Galvanic corrosion will readily occur on ships and submarines exposed to the marine environment, if two dissimilar metals are electrically coupled. This is the case because the electrolyte (seawater) is continuously present. An example of a system that may potentially experience galvanic corrosion is the steel hull of a submarine since it is galvanically coupled to the bronze propeller. A corrosion analysis must be made for the design of watercraft systems or else severe corrosion due to galvanic action in seawater may occur.

More localized galvanic corrosion may occur on metals such as aluminum alloys where copper ions exist. Copper is often present in different forms on-board watercraft; for example it is used in seawater handling systems and as antifouling coatings. Thus it may ionize and deposit on the aluminum, ultimately resulting in a galvanic cell causing localized galvanic corrosion of the aluminum.

5.2.3.4   Pitting Corrosion

Pitting is known to occur on passive, film-forming metals when they are exposed to stagnant or low-flow seawater. When pitting of passivated metals occurs the pits tend to be narrow and deep rather than wide and shallow.[11]

5.2.3.5   Stress Corrosion Cracking

Marine structures have inherent material flaws that may be targeted for stress corrosion cracking. Pits from pitting corrosion or material flaws, such as cracks caused by welding, act as initiation sites for stress corrosion cracking. Therefore, it is extremely important to the structural integrity of the system that the material is highly resistant to stress corrosion cracking in seawater.

5.2.3.6   Selective Leaching/Dealloying

Selective leaching of aluminum or dealuminization in aluminum bronze alloys used for seawater piping systems may occur aboard watercraft. In addition, dezincification may also occur in brass components of shipboard systems. These specific forms of dealloying may be very difficult to detect until failure of the component occurs.

5.2.3.7   Corrosion Fatigue

Failure of a metal due to corrosion fatigue will occur in fewer cycles in a seawater or marine environment than in a less corrosive environment such as air. Figure 50 shows how the fatigue limit of a component is reached much faster in a corrosive environment such as seawater as opposed to a relatively inert environment.
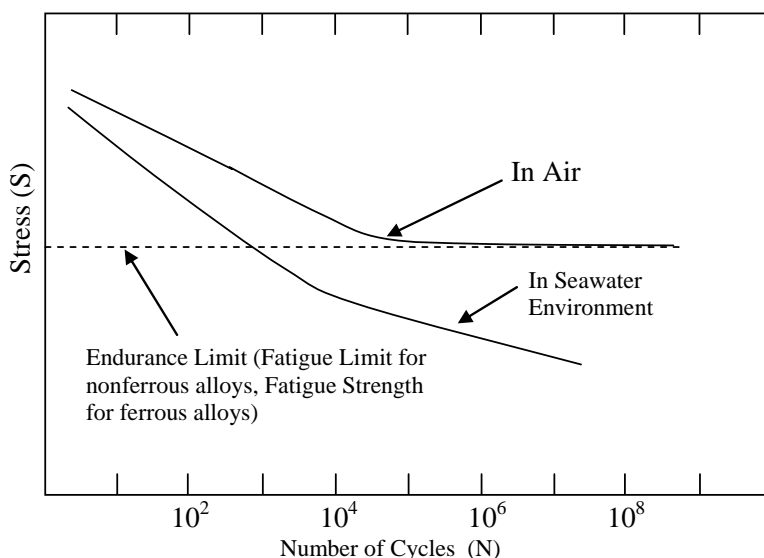
Figure 50   S-N Curve for a Metal Component Exposed to Air and a Similar One Exposed to Seawater[11]

5.2.3.8   Microbiological Corrosion

Bio-fouling can cause corrosion of watercraft in a few different ways. It can wear away or damage protective coatings, reduce the efficiency of the cathodic protection system, produce harmful environments such as H_2S, or increase drag and therefore stress, thus increasing the propensity for stress corrosion cracking on the watercraft's structure.

Microbial influence has been shown to have a significant effect by accelerating corrosion of stainless steel (e.g. 304L, 316L, AL-6XN), nickel alloy (e.g. alloy 400) and copper alloy (e.g. 90-10 Cu-Ni) weldments. It also has an effect but to a lesser extent on the corrosion of low-alloy steel weldments (e.g. HY-80 and HSLA-80). Conversely, microbial influence inhibits corrosion on aluminum alloy (Al 5086) and titanium weldments.[51]

5.2.3.9   Hydrogen Embrittlement

Weldments are common in the ship and submarine structures, but are especially susceptible to hydrogen embrittlement. The high temperature environment caused by welding can breakdown molecules such as hydrocarbons and produce hydrogen (atomic or molecular), which can then diffuse into the metal and initiate embrittlement. Thus, proper cleaning of the metal surfaces before welding to remove handprints, grease, paint or solvents will reduce the potential for hydrogen contamination and ultimately hydrogen embrittlement.[11]

5.2.3.10   Erosion Corrosion

The form of corrosion induced by flowing seawater is usually erosion corrosion. Metal corrosion typically increases with increasing seawater (relative) velocity until it reaches a critical velocity where the deterioration is much more rapid. Metals or alloys that have barrier films typically experience an accelerated rate of corrosion when exposed to flowing corrosion. Metals that form passive films, however, are generally more resistant to corrosion in flowing seawater. This is attributed to the presence and abundance of dissolved oxygen, which helps to continuously support the passive, protective film, but eats away the barrier film. For example, the design velocity for a barrier-film forming alloy might be 6-10 f/s, while that for a passive-film forming alloy might be greater than 100 f/s.[11] These passive film alloys, however, may be susceptible to severe localized corrosion in ambient seawater.

Salinity, dissolved oxygen concentration and inert contaminants all contribute to the extent and rate of erosion corrosion. Typically, erosion corrosion is greater with metals that are exposed to seawater with higher salinity than to those that are in a brackish (lower salinity) or fresh water environment; thus, erosion corrosion varies with salinity.[11] Finally, inert contaminants such as silt or sand may also accelerate the rate of erosion corrosion, even though they may only contribute to the mechanical (erosive) aspect of this form of material degradation.

A more specific form of erosion corrosion that typically occurs on the propellers of ships and submarines is caused by cavitation. Cavitation can enhance the erosive capability of the seawater that is moving, due to the extreme fluid phenomena that occurs at and near the surface of the blade. A propeller's rotational motion can result in a high relative velocity of the seawater moving over the propeller blades, which causes cavitation to occur. The formation and immediate collapse of vapor bubbles (cavitation) repeatedly hitting a particular location will often result in surface damage on the propeller. This specific form of corrosion may also occur

in other components that are in contact with water that cavitates. A key to preventing a significant amount of erosion corrosion is designing the component or system to minimize turbulence and cavitation.

5.2.3.11 High Temperature / Hot Corrosion

High temperature or hot corrosion can occur onboard watercraft, primarily in the engine components, for example, gas turbine engines. The turbine blades made of nickel and cobalt based superalloys have been known to experience this accelerated form of corrosive attack and severe material deterioration.

5.2.4 Types of Metals used in Watercraft

The construction materials for watercraft are usually chosen for their mechanical and structural properties rather than on their corrosion resistance. The dangerous consequence to this method of material selection is obvious, especially when considering that the intended operating environment is in seawater.

Past studies have grouped engineering alloys that are used in marine applications into five groups, which includes three groups of passive film-forming metals and two groups of barrier film forming metals.[11] The passive film-forming metals (Groups 1-3) typically have thin oxide films that form and provide protection in several different environments. These films provide good protection of the base metal from corrosion especially because they usually strongly adhere to the metal's surface. The barrier film-forming metals (Groups 4-5) typically have thicker films of corrosion product that form on the surface of the metal. Corrosion behavior of each group is described in more detail in Table 39. (The corrosion resistance as described for each of these groups are general observations which are not necessarily true for each alloy under all circumstances. Some alloys are susceptible to specific forms of corrosion under specific conditions, and it is prudent to consult the literature to evaluate how a material will behave in the intended environment.)

5.2.4.1 Group 1

Group 1 contains alloys that form passive films and have a characteristically high resistance to corrosion when immersed in seawater. Essentially, they form passive films that retain their integrity when exposed to seawater and are not easily penetrated by chloride ions. Thus, they are resistant to localized corrosion, such as pitting, and crevice corrosion in conditions where the seawater is stagnant or has a minimal velocity. Furthermore, because of their supreme ability to maintain a protective film in severe conditions, these alloys are highly resistant to erosion corrosion, even at high seawater velocities (>100 f/s). These alloys are well suited for use in marine applications with the exception of Ti-6Al-4V which is very susceptible to SCC in seawater. This group includes titanium and its alloys as well as several stainless steels and nickel-based alloys that have special formulations making them resistant to corrosion in the marine environment. Table 39 provides more details of the corrosion behavior of the alloys in this group.

5.2.4.2   Group 2

Group 2 contains alloys that also form passive films when exposed to seawater. Unlike the passive films formed on Group 1 alloys, however, Group 2 alloys are susceptible to penetration by chloride ions and localized breakdown in the passive film. The result is this group of alloys is susceptible to localized and crevice corrosion in ambient or low-velocity seawater. Generally, though, the corrosion resistance of the Group 2 alloys is satisfactory in intermediate to high-velocity seawater. The alloys in this group, in general, are also resistant to stress corrosion cracking and hydrogen embrittlement in seawater. An exception to this is when cathodic protection is applied to the higher-strength alloys (e.g. 17-4 PH) they may be susceptible to hydrogen embrittlement.

This group includes several stainless steels and nickel-based alloys. Of all the alloys in Group 2, type 304 SS is the least resistant to corrosion in seawater. Alloys from this group may be useful in applications that require a small area to be galvanically coupled to a less noble metal with a larger area. For example, Group 2 SS fasteners could be used to attach zinc sacrificial anodes to the ship or submarine structure. Another reasonable application for the Group 2 alloys is for rotational components, such as impellers in pumps. Under these applications, the alloy would then be exposed to high velocity seawater, which would enhance its resistance to corrosion. Table 39 provides more details of the corrosion behavior of the alloys in this group.

5.2.4.3   Group 3

Group 3 contains aluminum alloys, which form passive films when exposed to seawater. This group of alloys has limited application (especially the 2000-series alloys) for use on ships and submarines, since they are very susceptible to rapid degradation when the passive film is absent or removed. Table 39 provides more details of the corrosion behavior of the alloys in this group.

5.2.4.4   Group 4

Group 4 contains copper alloys. These alloys form thick barrier films and exhibit very good resistance to corrosion under stagnant or low-velocity seawater conditions. At moderate to high seawater velocities, however, they are much more susceptible to corrosion. The alloys in this group are commonly used for seawater handling systems. Table 39 provides more details of the corrosion behavior of the alloys in this group.

5.2.4.5   Group 5

Group 5 contains steels. These form thick barrier films, and in stagnant or low velocity seawater conditions these alloys are anywhere from moderately to very susceptible to corrosion. If the low to mild alloy steels in this group are used for surface ship or submarine applications they must be protected using a corrosion prevention method. The steels in this group are very susceptible to erosion corrosion in intermediate to high-velocity seawater. Table 39 provides more details of the corrosion behavior of the alloys in this group.

Table 39   Seawater Corrosion Behavior of Selected Engineering Alloys[11]

Performance Categories	Alloy Designation	Typical High Velocity Performance (>100 f/s) Uniform Corrosion Rate, mpy	Typical Intermediate Velocity Performance (25 f/s) Uniform Corrosion Rate, mpy	Threshold Velocity, f/s*	Typical Low Velocity Performance (0.2 f/s) Uniform Corrosion Rate, mpy	Bold Surface Pitting, Max. Depth, mils	Inside Crevice, Max. Depth, mils	Outside Crevice, Max. Depth, mils	Typical Stress Corrosion Performance	Remarks
Group 1 - Passive Film Alloys	AL-6X	0	0	>100	0	0	0	-	Most alloys in this group are resistant. Some Ti alloys require composition/processing control to minimize susceptibility	Excellent corrosion resistance at all seawater velocities
	IN-862	0	0	>100	0	0	0	-		
	Hastelloy C-276	0	0	>100	0	0	0	-		
	IN-625	0	0	>100	0	0	0	-		
	Multiphase MP35N	0	0	>100	0	0	0	-		
	Titanium and its Alloys	0	0	>100	0	0	0	-		
Group 2 - Passive Film Alloys	AISI 304L	0	0	>100	-	70 (1 year)	125 (1 year)	-	Resistant	Excellent corrosion resistance at intermediate and high velocities; localized attack at low velocities and inside crevices
	AISI 316L	0	0	>100	-	40 (1 year)	125 (2 years)	-	Resistant	
	Alloy 20 Cb-3	0	0	>100	-	10 (1 year)	90 (2 years)	-	Resistant	
	17-4 PH	0	0	>100	-	8 (1 year)	55 (2 years)	-	Possible susceptibility to HE	
	ACI CF-3M	0	0	>100	-	-	60 (1 year)	-	Resistant	
	ACI CN-7M	0	0	>100	-	-	60 (1 year)	-	Resistant	
	Nickel Alloy 200	0	0	>100	-	-	100 (2 years)	-	Resistant	
	Monel Alloy 400	0	0	>100	-	220 (2 years)	30 (2 years)	-	Resistant	
	IN-600	0	0	>100	-	130 (2 years)	130 (2 years)	-	Resistant	
Group 3 - Passive Film Alloys	AA 3002	Poor	-	-	0	0	-	0	Lower strength alloys (3000 and 5000 series) - resistant	No Consistent Behavior at low velocities and stagnant conditions; susceptible to degradation by erosion-corrosion at high velocities. In general for aluminum alloys - composition and temper must be carefully selected to minimize pitting, crevice corrosion and other forms of attack.
	AA 5086	Poor	Satisfactory	-	1.2	0.2 (1 year)	-	0.2 (1 year)		
	AA 5456	Poor	Satisfactory	-	1.2	0.2 (1 year)	-	0.2 (1 year)		
	AA 2024	Poor	-	-	-	35 (1 year)	-	49 (1 year)	Higher strength alloys (2000, 6000 and 7000 series) - resistance related to composition and temper	
	AA 6061	Poor	-	-	-	60 (1 year)	-	11 (1 year)		
	AA 7075	Poor	-	-	-	66 (10 years)	-	16 (1 year)		
Group 4 - Barrier Film Alloys	Naval Brass (CA 464)	-	-	10	0.26	-	-	-	Alloys in this group are resistant	Moderate to excellent corrosion resistance at low velocities and stagnant conditions; susceptible to degradation by erosion-corrosion at intermediate and high velocities. Naval Brass (CA 464) may be susceptible to dealloying (dezincification). The aluminum bronze alloys (CA 952 and CA 958) may be susceptible to dealuminization.
	G-Bronze (CA 902)	30	10	12	2	-	-	-		
	Aluminum Bronze (CA 952)	50	19	15	0.2	-	-	Trace		
	Nickel Aluminum Bronze (CA 958)	30	10	14	2	-	-	Trace		
	90/10 Copper Nickel (CA 706)	35	12	12	0.5	-	-	Trace		
	70/30 Copper Nickel (CA 715)	60	22	15	0.5	-	-	Trace		
Group 5 - Barrier Film Alloys	AISI 1020 Steel	300	35	5	7	-	-	-	Steels over 100 ksi yield strength require composition, processing and design control to circumvent stress corrosion problems	Poor to moderate corrosion resistance at low velocities and stagnant conditions; highly susceptible to degradation by erosion-corrosion at intermediate and high velocities.
	HTS Steel	-	-	5	9	-	-	-		
	HY 80 Steel	-	-	5	9	-	-	-		
	HY 100 Steel	-	-	5	9	-	-	-		
	HY 130 Steel	-	-	5	7	-	-	-		

Note – The quantitative data reported were arrived at by normalizing the results from many exposure programs in various ocean environment locations. Generally, high velocity exposures – 30 days duration; intermediate velocity exposures – 60 days duration; stagnant or low velocity exposures – 1 year or more duration.

He – Hydrogen Embrittlement

A "-" indicates that there was no available data.

* When a metal is exposed to flowing seawater at a very low relative velocity, the rate at which corrosion occurs increases moderately with velocity. Once the relative seawater velocity reaches the metal's threshold velocity the dominating corrosion mechanism becomes erosion corrosion, the rate of which increases dramatically as a function of velocity.

5.2.4.6   Stainless Steels

Stainless steels exposed to seawater are susceptible to severe corrosion, especially localized attack in the form of pitting and crevice corrosion. In general, SS is more susceptible to corrosion in seawater with higher chloride content, higher oxygen content, lower pH and higher temperature.

Some alloy formulations, however, do exhibit good corrosion resistance properties in seawater. AL-6X and IN-862 stainless steels, for example, exhibit good resistance to SCC and hydrogen embrittlement. These particular alloys are part of Group 1 in Table 39.

Group 2 stainless steels are less resistant to corrosion in seawater than those in Group 1. Type 316 SS is generally more resistant to the initiation of corrosion than the 304 alloy, and alloy 20 Cb-3 has a slightly better corrosion resistance than 17-4 PH SS. Localized attack is a vulnerability in these SS, especially when they are operated in seawater over long periods.

5.2.4.7   Low- and Mild-Alloy Steels

Low to mild alloy steels are not inherently resistant to marine environments. That is, they must be used in conjunction with a corrosion prevention and control method since they are very susceptible to corrosion in these environments. These steels are often used as the hull and structural components of surface ships and submarines. This is primarily because they are relatively inexpensive and have suitable welding, strength and other properties. On the galvanic series chart in seawater, low- and mild-alloy steels are near the bottom (anodic) and thus are prone to galvanic corrosion if coupled with a more cathodic-acting metal. Of course, since they are often used as large area components, this is not as severe of a corrosion problem as it might be otherwise. Low and mild alloy steels are resistant to SCC in seawater.

5.2.4.8   Nickel-Based Alloys

Hastelloy C-276, Inconel-625, and MP35N nickel-based alloys exhibit a good resistance to SCC and hydrogen embrittlement. Nickel-based alloys, such as Nickel Alloy 200, Monel Alloy 400 and Inconel-600 are susceptible to localized corrosion in seawater, similar to the Group 2 SS. Monel and Inconel 625 are sometimes used for valves and pumps aboard watercraft.[11] These particular alloys are part of Group 1 in Table 39.

Inconel alloy 686 is a nickel-based alloy which offers high strength, ductility, toughness and corrosion resistance. Specifically, this alloy is resistant to fatigue, pitting, crevice corrosion, and SCC in seawater as well as hydrogen embrittlement. It has been suggested for use as a fastener material in applications subjected to the marine environment.[52]

5.2.4.9   Aluminum Alloys

Aluminum is oxidized rapidly in environments such as seawater, and therefore, it forms a protective layer very quickly. However, if the film cannot be maintained, the aluminum may suffer rapid deterioration. Corrosion resistance of aluminum alloys in stagnant or low-velocity seawater varies in specific alloys. The susceptibility of aluminum to crevice corrosion is also dependent on the specific alloy.

The 2000-series of aluminum alloys, in general, are not suitable for use in marine environments since they are highly susceptible to corrosion. Depending upon temper the 6000- and 7000-series aluminum alloys exhibit a decent resistance to localized and crevice corrosion in seawater environments. The 3000- and 5000-series of aluminum alloys typically exhibit the best resistance to corrosion in seawater environments.

Aluminum alloys are near the bottom (anodic) portion of the galvanic series chart, and therefore, are very susceptible to galvanic corrosion in seawater when coupled with another more cathodic metal. Hence, unless they are used with a small cathode-to-anode ratio they should not be electrically coupled with a dissimilar metal. Furthermore, seawater containing heavy metal ions (e.g. Hg, Cu, Fe, etc.) can also create localized galvanic corrosion on aluminum. Ultimately, the applicability of aluminum and its alloys to ships and submarines is very restricted due to their susceptibility to corrosion.

5.2.4.10   Copper Alloys

Copper alloys can be used for applications that require exposure to the marine environment. They are generally resistant to localized and crevice corrosion in stagnant or low-velocity seawater. Copper-based alloys are typically used in seawater handling systems and machinery components. Copper-nickel alloys are used for piping and heat exchangers.[11] Seawater piping systems and heat exchangers aboard surface ships and submarines, for example, have used 70/30 Cu-Ni alloys. Bronze alloys, for example, are sometimes used for valves and pumps aboard watercraft.[11]

Cast nickel-aluminum-bronze (NAB) is commonly used as the propeller material on US Navy ships and submarines, as well as for valve bodies and pump casings. Bronze is used because it has a high-quality surface finish which reduces the amount of cavitation induced damage. Moreover, bronze contains copper which is good for preventing organisms from building up on the propeller, thus preventing microbiologically influenced corrosion. Even more reason for using bronze is that in general it has a good resistance to corrosion in seawater. One particular problem with using bronze as a propeller material is that it can cause corrosion problems for other metals that are galvanically coupled to it. For example, if there is an electrical path between the propeller and the ship/submarine hull, the steel used for the hull may experience accelerated corrosion.

5.2.4.11   Titanium

Titanium is an outstanding material for use in seawater environments, but it is susceptible to SCC and other cracking processes. To minimize this, very specific formulations of titanium can be used. Interstitials, such as oxygen, in Ti-6Al-4V, for example, must be maintained at a very low level to minimize resistance to SCC. Titanium is highly resistant to microbiologically induced corrosion especially sulfate-reducing bacteria, and is also highly resistant to crevice corrosion. Titanium is sometimes used for valves and pumps aboard watercraft.[11]

5.2.5   Corrosion Prevention and Control – Methods and Maintenance

There are a number of effective methods to impart inherent corrosion resistance to a system, even if it operates in the most severely corrosive environment experienced by surface ships and

submarines. These methods and materials, however, must be used and applied with care, otherwise they may not provide the required level of protection. In general, the methods used to prevent and control corrosion on surface ships and submarines include coatings and surface treatments, maintenance, cathodic protection, and design and material selection.

5.2.5.1 Coatings and Surface Treatments

Coatings and surface treatments for corrosion protection on surface ships and submarines include systems that act as barriers to the environment, provide chemical protection, or corrode preferentially. These typically include metal spray coatings, high performance organic and inorganic coatings, powder coatings, ceramic coatings, polysulfide sealants, antiseize compounds and vapor phase inhibitors.[11]

A barrier coating should possess the following characteristics in order to be effective in protecting the substrate from corrosion:

- Low or no permeability to moisture and oxygen
- Strong adhesion to the substrate
- Smooth and continuous application
- Good resistance to chemicals, abrasion and wear

A potential problem with coatings that act as sacrificial anodes (corrode preferentially) is that they are expended over time. That is, in order to protect they must corrode preferentially and as this occurs the coating is depleted and must subsequently be replaced. Some specific coating systems are described below.

Epoxy Polyamide Coatings: Epoxy polyamide coatings are two component coating systems that have traditionally been used on Navy submarines. These have been used on the exterior of the hull, in tanks, and on other interior areas of the submarine. Some of the characteristics of epoxy polyamide coating systems are provided in Table 40.

Table 40   Characteristics of Epoxy Polyamide Coating Systems for Surface Ship or Submarine Applications[11, 53]

Advantages	Disadvantages
Excellent chemical and solvent resistance	Two-package* coating – limited pot life
Excellent water resistance	Curing temperature must be above 50°F
Very good exterior durability	Poor gloss retention
Hard, slick film	Film chalks on aging
Excellent adhesion	Blasted surface desirable
Excellent abrasion resistance	For recoating, can only be applied over epoxy or polyurethane. Otherwise surface may require abrasive blasting or solvent paint remover.
Good caustic resistance	

*Two-package coating consists of epoxy component and a polyamide component which must be mixed together.

Vinyl Coatings: Vinyl coatings are single component coatings that provide excellent corrosion resistance in both fresh water and seawater environments. They have been used as anti-fouling coatings on submarines. Some of the characteristics of vinyl coating systems are provided in Table 41.

Table 41　　Characteristics of Vinyl Coating Systems for Surface Ship or Submarine Applications[11]

Advantages	Disadvantages
Rapid drying and recoating	Poor solvent resistance
Excellent chemical resistance	Poor heat resistance
Excellent fresh and salt water resistance	Low film build per coat
Excellent durability	Poor adhesion
Very good gloss retention	Poor tolerance of moisture during application
Applicable at low temperatures	
Excellent acid and alkali resistance	

Alkyd Coatings: Alkyd coatings are single component coatings that have been used as primers and topcoats on the interior of submarines. Modified alkyds such as weather-resistant silicone-alkyds have been used on topside areas of surface ships, and chlorinated alkyds are fire retardant. Some of the characteristics of alkyd coating systems are provided in Table 42.

Table 42　　Characteristics of Alkyd Coating Systems for Surface Ship or Submarine Applications[11]

Advantages	Disadvantages
Single component coating	Poor chemical and solvent resistance
Fair exterior durability	Fair weather resistance
Moderate cost	Poor heat resistance
Excellent flexibility	Poor immersion resistance
Good adhesion to most surfaces	
Easy to apply	
Good gloss retention	

Inorganic Zinc Coatings: Inorganic zinc-rich coatings are sacrificial coatings that contain a high zinc content, which corrodes preferentially, thus providing corrosion protection to the substrate. Some of the characteristics of inorganic zinc coating systems are provided in Table 43.

Table 43   Characteristics of Inorganic Zinc Coating Systems for Surface Ship or Submarine
Applications[11]

Advantages	Disadvantages
Offers one-coat protection under many service conditions	High cost
Excellent exterior durability	Spray application only; skilled applicators required for successful job
Excellent heat resistance	Not suitable for acidic or caustic service unless properly topcoated
Excellent abrasion resistance	Requires careful selection of tie coats and topcoats for service involved
Provides galvanic protection properties	Selected temperature and humidity effects, depending on the type used
Provides permanent primer capability when used in conjunction with proper topcoats and/or maintenance practices	Constant stirring necessary
Good resistance to immersion in oils and organic solvents	Long cure time; avoid moisture during initial cure time (one hour)
Can be made self-curing	

Nonskid Deck Coatings: Nonskid deck coatings are used for two purposes. They are used as friction surface for vehicles and personnel to be able to move and walk on the deck without sliding. The coating also provides protection of the surface of the ship from corrosion.

Metal Spray Coatings: For shipboard or submarine systems that are exposed to high heat (>175°F), high humidity and salt spray, metal spray coatings can be used to provide protection. Aluminum is a common material applied as a metal spray to protect against corrosion. Aluminum coatings protect steel by separating it from corrosive environments and additionally, acting as a sacrificial anode. Moreover, an epoxy or high temperature sealant can be applied directly over the aluminum to provide extra protection. The service life of such a coating system is expected to be greater than 7 years in most systems.[11] These systems are intended for use on steel or aluminum alloy substrates. Below is a list of surfaces that metal spray coatings should not be used on.[11]

- Internal surfaces of moving machinery (e.g. pump casings, valves)
- Brass, bronze, nickel-copper, or Monel surfaces
- Stainless steels
- Surfaces subject to strong acids or bases
- Threads of fasteners
- Valve stems
- Within ¾ inch of surfaces to be welded
- Steel alloys with yield strength greater than 120,000 psi
- Nonskid deck coatings
- Exterior hull surfaces
- Interior of sanitary tanks
- Plastic, rubber, or painted surfaces

Powder Coatings: Powder coatings are useful to protect systems and areas that have little access for maintenance and/or are exposed to severe moisture, wear or abrasion. These are strongly adherent coatings that provide a thick barrier and prevent moisture penetration. Some examples of powder coatings are polyvinyl chloride, polyethylene, polyester, epoxy, acrylic and nylon.

Vapor Phase Inhibitor: Vapor phase inhibitors (VPI) are used to protect iron and aluminum alloys against corrosion in systems that operate in stagnant air conditions, such as in lockers or small containers. They form a highly protective, molecular film when exposed to air.

Polyurea Coatings: Polyurea coatings are used to protect steel from corrosion in the severe marine environment. They are useful for areas or components where only minimal surface preparation can be achieved. High tensile strength, flexibility and impact resistance are among some of the good mechanical properties that polyurea coatings possess.[54] Moreover, polyurea has a fast reaction time and is generally resistant to the effects of chemicals, high humidity and temperature. Polyurea can withstand temperatures as high as 250°F and humidity levels greater than 90% without suffering long-term effects. If surface preparation and application processes are done well, it can provide corrosion protection for over 10 years.

CPCs and Anti-fouling Coatings: Corrosion preventive compounds are also used for corrosion protection of ships. Some examples of CPCs are listed in Table 87 in Section7.3.3.1. Anti-fouling coatings are usually used on exterior surfaces of ships and submarines to protect against corrosion resulting from bio-fouling. These coatings inhibit the attachment of barnacles, grass, algae, as well as other marine growth. These coatings usually contain copper which acts as a biocide or toxicant, or organo-tin compounds.

5.2.5.2 Cathodic Protection

On submarines and surface ships the primary use of cathodic protection is for the protection of steel against corrosion. When protecting the hull, internal tanks, and free flood spaces, CP is most often used in conjunction with other protection methods such as coatings. The reason for the combination of protection methods is to provide a redundancy or backup in protection, where the CP system is the backup if the coating fails. In effect, this prevents against severe localized corrosion that might otherwise result in a catastrophic failure. Impressed current CP has traditionally been used on surface ships, while sacrificial anodes have traditionally been used for submarines. Magnesium, zinc or aluminum is often used for the sacrificial anode onboard these watercraft. For sacrificial anodes to work effectively they require an electrolyte, thus they usually require immersion in seawater. Generally, in seawater environments, any alloy that is more anodic than the alloy to be protected according to the galvanic series (see Table 19) may be used for cathodic protection.

A side effect of cathodic protection of systems that operate in seawater is the deposition of calcium magnesium and strontium salts on the surface of the metal being protected. These, however, are not directly harmful to the metal. Corrosion control experts should be consulted for applying cathodic protection systems, since achieving a proper level of protection by this method is very complicated.

Sacrificial anodes are also used to protect submarine propellers, bilge areas, ballast tanks, sonar domes, and stern tubes. Sacrificial anodes, however should not be *attached* to propellers, propeller shafts, or rudders.[11] Aluminum sacrificial anodes have been used to protect periscope

housings on submarines. Zinc anodes are used for machinery such as heat exchangers, condensers, and evaporators. Bolt-on and weldable anodes are available, but the bolt-on type is replaceable.

5.2.5.3   Maintenance

One of the most effective methods in preventing corrosion from seawater is to routinely wash the components with fresh water in order to rinse away all the salt and chloride products. Also, routine maintenance and inspection of specific components is a good way to prevent or identify corrosion problems prior to them causing more serious concern and damage.

5.2.5.4   Design and Material Selection

A fundamental method to protect against corrosion aboard ships and submarines is to perform proper material selection during design. Ships and submarines use steel as the primary structural material, primarily due to its relatively low cost and good strength, durability and shock resistant properties. The use of improved fastener materials is a good way to prevent corrosion generally found on joints. Since welding is a very common practice in shipbuilding, it is extremely important that the metals used have good weldability characteristics; otherwise the welded joints will be especially susceptible to corrosion.

Design flaws can also lead to severe corrosion of specific components. Some of the common design deficiencies in systems that are exposed to wet, humid or salt spray environments are provided in Table 44.

Table 44   Design Deficiencies that May Lead to Corrosion Problems in Marine Environments[11]

Lack of adequate or poorly installed drainage, resulting in standing water.
Location of components and structures in such close proximity that inaccessible areas are created where maintenance is difficult or impossible.
Combinations of dissimilar metals in areas exposed to salt water and spray. In some instances inadequate dielectric insulation is provided between the two metals.
Selection of metal shapes that are functional for their primary purpose but create corrosion-maintenance problems by their complex form or shape.
Use of commercial fixtures or fittings that, because of their construction or material, were not intended nor suitable for use in a marine environment.
Use of fastener systems that combine bolts, nuts, and washers of dissimilar metals and are used to join dissimilar metals.
Use of absorbent materials, such as insulation, in exposed areas.

Ultimately, proper material selection and design for corrosion resistance will significantly reduce life-cycle and maintenance costs. Therefore, appropriate consideration of these aspects prior to

ship and submarine building will greatly enhance the mission readiness of these critical military vessels.

5.2.6 Corrosion Inspection and Monitoring

See Section 8.0 for information on inspection and monitoring methods.

5.3 Ground Vehicles

The military possesses a vast number of ground vehicles serving many different purposes and operating in a variety of environments. These vehicles, whether they are tactical, amphibious, attack, transport or cargo vehicles, are all prone to corrosion, if they are not properly designed, manufactured and maintained. In general, there has been little effort on corrosion prevention and control of the Army's fleet of ground vehicles. Figure 51 shows an example of corrosion on the body and in the door of a 5-ton Army truck.
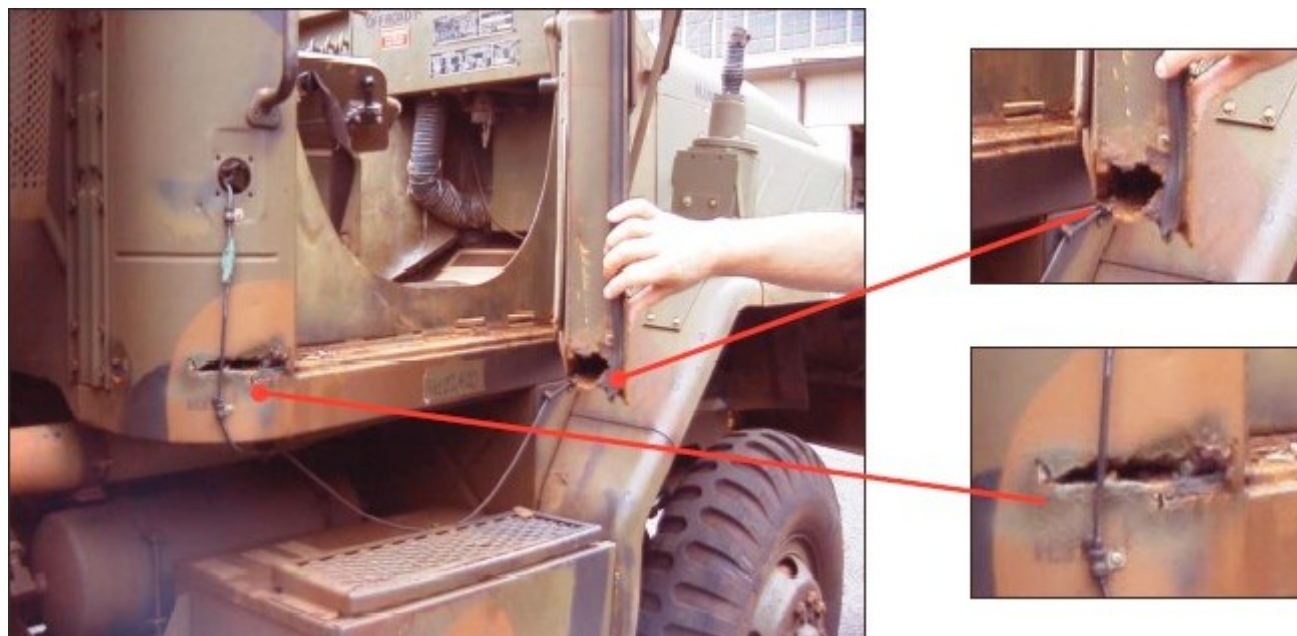
Figure 51   Corrosion on a 5-Ton Army Truck in Hawaii[42]

5.3.1 Typical Corrosive Environments

Ground vehicles may be exposed to a variety of environments, ranging from severe to relatively passive in terms of corrosion. Marine, industrial, and desert environments are all commonly encountered by military ground vehicles. Amphibious vehicles, such as the Advanced Amphibious Assault Vehicle (AAAV) – now known as the Expeditionary Fighting Vehicle (EFV), by definition are intended to operate both on land and in water, thus in both dry and wet conditions. Some of the conditions encountered by ground vehicles include high humidity, salt spray, road deicing agents, gravel and sand impingement, atmospheric contamination, and temperature extremes. Ground vehicles may encounter splash and salt spray if they are being transported on a ship. In addition, amphibious vehicles can also encounter salt spray during

operation. Non-amphibious ground vehicles, such as tanks, are exposed to water and even seawater when being transported aboard ships.

Climate has a significant impact on the degree of corrosion exhibited by ground vehicles. For example, locations near the ocean are exposed to higher amounts of chlorides from the atmosphere. Furthermore, rainfall and higher temperatures will result in higher rates of corrosion. Besides being in or near an ocean environment, one of the more severely corrosive environments encountered by ground vehicles is wintery roadway conditions, where salt is used to melt ice and snow. This salt combined with the moisture from the snow and ice as they melt creates a very corrosive medium that readily attacks metal components on vehicles. Hot, coastal environments present another very corrosive environment. The humid, salt air and high temperatures cause an acceleration of corrosion. Corrosion in environments near the ocean can be 400-500 times greater than in desert environments.[55]

Polluted environments in urban or industrial areas can have a significant impact on the rate of corrosion on automobiles. Industrial contaminants such as sulfur dioxide generally act to increase the rate of corrosion on exposed metals.

5.3.2   Major Components Susceptible to Corrosion

While rust is familiar to the body of virtually all older and even some newer automobiles, corrosion also takes place in other components of ground vehicle systems. Drive shafts, transfer cases, differentials and exhaust systems are very susceptible to corrosion, primarily due to their under-body position on the vehicle. Table 45 provides corrosion data that was compiled from an audit on the extent of corrosion in Military ground vehicles.

Table 45   Results from a Corrosion Inspection Study on Military Ground Vehicles[56]

Vehicle Type	No. of Vehicles Inspected	No. of Sites Visited	Average No. of Corroded Parts Per Vehicle	Average Age of Vehicles (In Years)
HMMWV	121	7	48	4.7
M-900	57	11	55	5.7
HEMTT	9	3	151	3.1
Crane	3	3	27	1.3
Flatbed	62	6	25	9.2
Tankers	11	4	25	6.3
Forklifts	12	8	24	4.6
Total	275	17*	51	5.9

* The number of sites visited is not the sum of the column, since there is not a 1 to 1 correlation between sites and types of vehicles (e.g. most sites had more than one type of vehicle).

Some areas of military vehicles that commonly experience corrosion include the high temperature areas on the engine and exhaust systems. Most corrosion on Military ground vehicles is found near or on screws, bolts, fasteners, bumpers and tie-down supports, the vehicle body, passenger compartments, body frames, suspension components, and engine compartments. Some specific parts on ground vehicles that have shown to be susceptible to corrosion are given in Table 46.

Table 46   Ground Vehicle Components Commonly Susceptible to Corrosion[56]

Vehicle Component	No. of Vehicles Affected (out of 275)	Percentage Affected
Engine Compartment		
Heads	49	17.8
Injectors	53	19.3
Engine Mounts	78	28.4
Valve Covers	87	31.6
Radiator Assembly	131	47.6
Suspension and Steering		
Idler Arms	48	17.5
Control Arms (HMMWV only)	78	28.4
Tie Rod	124	45.1
Housing, Axle	161	58.5
Springs	205	74.5
Body		
Fenders	72	26.2
Bumpers	105	38.2
Door Frames	115	41.8
Bed	120	43.6
Tie Downs/Lift Points	209	76.0
Underbody		
Metal Brake Lines	35	12.7
Air Tanks	40	14.5
Driveshafts	105	38.2
Fuel Lines	106	38.5
Universal Joints	135	49.1
Other		
Pump Assembly (HEMTT and Tankers	13	4.7
Forklift and Crane Assemblies	22	8.0
Metal Hydraulic and Air Line Connections	25	9.1
Welded Seams	73	26.5
Fuel Tank Assemblies	135	49.1
Nuts, Bolts, and Fasteners	177	64.4
Frame	187	68.0

A buildup of water or moisture and deposits is commonly the cause of corrosion on ground vehicles. The frame of the HMMWV, hatch areas of the Light Armored Vehicle (LAV), weldments on trucks and trailer beds, and battery boxes for trucks, are some examples.[59]

The HMMWV, although viewed as a generally successful vehicle for the US Military, has had a history of corrosion problems. A review of the design of the HMMWV has lead to a number of obvious corrosion prone areas.[57] For example,

- The use of 1010 carbon steel without galvanizing or protective coatings

- Holes in the side of the steel frame, which lets water in, but no holes in the bottom to let water out.

- Coupling of dissimilar metals, such as rivets

- Out-dated coating procedures

- Use of poor protective coatings

Table 47 provides a list of some specific corrosion prone areas on the HMMWV and the corresponding material as well as the form of corrosion.

Table 47   HMMWV Corrosion Sites and Mechanisms[55, 58]

Location	Component	Material	Corrosion Form
Engine Compartment	Wiring harness control box	2024-Aluminum	Crevice
	Headlight connectors	Cd-plate 2024 Al	Crevice
	STE-ICE connectors	Cd-plate 2024 Al	Crevice
	Radiator	Multiple	Uniform
Underside	Brake rotors	1010 Steel	Uniform
	Drive lines	1010 Steel	Uniform
	Transfer mounts	1010 Steel	Uniform
	Suspension bolts	1010 Steel	Uniform
	Vehicle frame	1010 Steel	Pitting
Exterior	Headlight brackets	1010 Steel	Galvanic
	Battery boxes	1010 Steel	Uniform
	Exhaust pipes	Steel	Uniform

Amphibious and light armor vehicles have been known to have corrosion problems caused by seawater leaking through turret areas.[59] The interior connectors, fittings, fasteners, hydraulic lines, control boxes, etc. were consequently corroded since they were not intended to be exposed to seawater. Vision blocks on the turrets of amphibious and light armor vehicles have corroded due to a consistently poor application of sealant.

Some of the areas susceptible to corrosion on the Amphibious Assault Vehicle (AAV) include the engine compartment and the interior and exterior of the vehicle. The engine compartment of the AAV has exhibited corrosion problems with a number of components including electrical

connectors, hydraulic fittings, the starter, radiator, and steering and brake linkages. Most painted components exhibited a significant loss of paint including the fuel/water separator. Table 48 provides a list of some specific corrosion prone areas on the AAV and the corresponding material as well as the form of corrosion.

Table 48　　　AAV Corrosion Sites and Mechanisms[55]

Location	Component	Material	Corrosion Form
Engine Compartment	Electrical fittings	Aluminum, Steel	Uniform and Crevice
	Electrical connectors	Aluminum, Steel	Uniform and Crevice
	Steering linkages	Steel	Uniform
	Brake linkages	Steel	Uniform
	Starter connections	Steel	Uniform
	Radiator grills	Multiple	Uniform
	Fuel/water separator	Steel	Uniform
	Fuel lines	Cu-plate steel	Uniform
	Hydraulic solenoids	Multiple	Galvanic
Interior	Blower assemblies	Multiple	Crevice
	Personnel heaters	Steel	Uniform
	W3P6 electrical connectors	Cd-plate aluminum	Uniform and Crevice
Exterior	Electrical connectors	Cd-plate aluminum	Uniform and Crevice
	Vision block frames	Steel	Crevice
	Armor plates	Steel	Crevice
	Cd-plated bolts	Steel	Uniform
	Track tension adjuster piston	Cd-plate steel	Pitting

The Light Armored Vehicle (LAV) also has a number of corrosion problems. The tie rods, for example had exhibited significant corrosion and in some instances had fractured. Steel fuel lines, aluminum electrical connectors, and mild steel support brackets for the periscope are other components on the LAV that have been susceptible to corrosion. Table 49 provides a list of some specific corrosion prone areas on the LAV, and the corresponding material as well as the form of corrosion. Table 50 through Table 53 have similar data for other land vehicle systems.

Table 49   LAV Corrosion Sites and Mechanisms[55]

Location	Component	Material	Corrosion Form
Engine Compartment	Electrical fittings	Aluminum, steel	Uniform and Crevice
	Connectors	Aluminum, steel	Uniform and Crevice
	Fuel lines	Cu-plate steel	Uniform
	Crossover coolant pipes	Aluminum	Uniform and Crevice
Interior	Slew brake	NA	Uniform
	Transversing brake	NA	Uniform
	Connectors	Aluminum, steel	Uniform and Crevice
Exterior	Vision block frames	Steel	Uniform and Crevice
	Electrical connectors	Cd-plate aluminum	Uniform and Crevice
	Periscope brackets	Steel	Uniform
	Hatch areas	Steel	Uniform and Crevice
	Headlights/turn signals	Steel	Uniform and Crevice

NA – Not Available

Table 50   Logistics Vehicle System (LVS) Corrosion Sites and Mechanisms[55]

Location	Component	Material	Corrosion Form
Engine	Exhaust components	Steel	Uniform and Crevice
	Radiator grills	Multiple	Uniform
Interior	Cab frame	Steel	Uniform
Exterior	Cab frame	Steel	Crevice
	Door frame	Steel	Crevice
	Hydraulic reservoir cap	Steel	Uniform
	Hydraulic cylinder rods	Cr-plate steel	Pitting
	Battery boxes	Steel	Uniform
MK-17 Trailer	Trailer bed	Steel	Uniform
	Support frames	Steel	Crevice
Hydraulic Crane	Control boxes	Steel	Uniform
	Support frames	Steel	Crevice
Six-Con Pump Module	Support brackets	Steel	Uniform
	Storage boxes	Steel	Uniform

Table 51   Corrosion Sites and Mechanisms for M-800 and M-900 Series 5-Ton Trucks[55]

Location	Component	Material	Corrosion Form
Exterior	Cab doors	Steel	Crevice
	Windshield frame	Steel	Crevice
	Muffler pipes	Steel	Crevice
	Fuel tanks	Steel	Uniform
	Battery boxes	Steel	Uniform
	Hand brake	Steel	Uniform
	Welded frames	Steel	Crevice
	Storage boxes	Steel	Uniform and Pitting

Table 52   M1A1 Tank Corrosion Sites and Mechanisms[55]

Location	Component	Material	Corrosion Form
Engine Compartment	Transmission casing bolts	Cd-plate steel	Uniform
	Recuperator	NA	Uniform
	Steering cable	Steel	Uniform
	NBC unit fasteners	Cd-plate steel	Uniform
	Engine blades	NA	Erosion corrosion

NA – Not Available

Table 53   Corrosion Sites and Mechanisms for Miscellaneous Land Systems[55]

System	Component	Material	Corrosion Form
D7 Bulldozer	Fuel lines	Steel	Uniform
	Hydraulic lines	Cr-plate steel	Pitting
	Operator compartment	Steel	Uniform
1051 Bulldozer	Hydraulic lines	Cr-plate steel	Pitting
Container Handler	Corner clamps/connections	Steel	Uniform
Extended Boom Fork Lift	Cab door	Steel	Crevice
	Hydraulic pistons	Cr-plate steel	Pitting
MEP 5 Generator	Battery boxes	Steel	Uniform
ROWPU Water Purification Unit	Control nozzles and drains	NA	Uniform
	Electrical cabinet	NA	Uniform
RTCH	Non-skid floor panels	Steel	Uniform and Crevice
	Engine screen	Steel	Uniform
	Body panel supports	Steel	Crevice
	Exhaust systems	Steel	Uniform
30-Ton Crane	Cab panels	Steel	Uniform
	Radiator guards	Steel	Uniform
	Engine covers	Steel	Uniform
	Radiator	Multiple	Uniform
	Exhaust systems	Steel	Uniform and Pitting
M198 Howitzer	Shims on optic mechanism	Brass	Uniform
	Brake system	NA	Uniform

NA – Not Available

5.3.2.1   Fasteners

Cadmium-plated steel fasteners used for ground vehicles have been known to exhibit corrosion when the cadmium plating failed. The steel substrate is then rapidly attacked, and if the steel is in contact with another metal, it may consequently cause galvanic corrosion.

5.3.2.2   Electrical Connectors

Electrical connectors commonly experience corrosion aboard military ground vehicles. The main problem is often moisture or salt accumulating under locking collars and rubber seals and causing crevice corrosion. Electrical connectors should be fabricated from composite or 316 stainless steel overcoated with a sealant to maximize corrosion resistance.[59]

5.3.2.3   Fuel Tanks and Fuel Lines

Fuel tanks are exposed to a very corrosive environment, which can include fuel, contaminants from the fuel, condensed moisture, salt, and higher temperatures. Steel fuel lines have also been known to corrode on the Light Armored Vehicle (LAV). Protective coatings are commonly used to prevent corrosion on fuel systems in ground vehicles.

5.3.2.4   Exhaust Systems

The metals used in exhaust systems are subjected to some very severely corrosive environments, including high temperatures, harmful contaminants and chemicals. These systems may experience temperatures near 1600°F. For vehicles such as the HMMWV, aluminized 409 stainless steel exhaust systems should be used to minimize corrosion. Several exhaust systems installed on HMMWVs and 5-ton trucks were field tested for corrosion resistance in a marine atmospheric environment (Kure Beach, NC). Table 54 shows the results of these tests.

5.3.2.5   Engine

Various components within an engine are susceptible to corrosion, including electrical connectors and radiators.

Table 54   Results of Corrosion Field Testing of Exhaust Systems Installed on HMMWVs and M-900 Trucks[60]

Coating	Substrate	Vehicle	Component	Coating Performance	Substrate Performance
MIL-P-14105 (Heat Resistant Paint)	Aluminized Steel	M939 5-Ton Truck	Muffler	3	Stage 2
		HMMWV	Fording Kit	2	Stage 1
	409 Stainless Steel	HMMWV	Muffler	2	Stage 0
		HMMWV	Fording Kit	2	Stage 1
	Aluminized 409	HMMWV	Muffler	1	Stage 0
Ameron PSX 738 (High Temperature Siloxane Coating)	Aluminized Steel	M939 5-Ton Truck	Muffler	3	Stage 2
		HMMWV	Fording Kit	3	Stage 1
	409 Stainless Steel	HMMWV	Muffler	2	Stage 1
		HMMWV	Fording Kit	2	Stage 1
	Aluminized 409	HMMWV	Muffler	3	Stage 0
Ameron PSX 892 (High Temperature Siloxane Coating)	409 Stainless Steel	HMMWV	Muffler	2	Stage 1
	Aluminized 409	HMMWV	Muffler	4	Stage 0
Dampney Thurmalox (Heat Resistant, Protective Coating)	Aluminized Steel	M939 5-Ton Truck	Muffler	3	Stage 2
		HMMWV	Fording Kit	2	n/a
	409 Stainless Steel	HMMWV	Muffler	2	Stage 1
		HMMWV	Fording Kit	1	Stage 0
	Aluminized 409	HMMWV	Muffler	3	Stage 0
VHT 1200 (Flameproof Ceramic-Silicone Coating)	Aluminized Steel	M939 5-Ton Truck	Muffler	2	Stage 1
		HMMWV	Fording Kit	1	Stage 0
	409 Stainless Steel	HMMWV	Muffler	1	n/a
		HMMWV	Fording Kit	1	n/a
	Aluminized 409	HMMWV	Muffler	1	n/a

Coating Performance Ranking
1: No coating degradation
2: Isolated areas of coating loss < 10% of surface area
3: Coating loss 10 – 30%
4: Poor Coating loss in excess of 30%

Substrate Ranking – condition of uncoated substrate
n/a: not applicable, no bare metal exposed

Stage 0: no rust

Stage 2: lightly rusted, may have loose, powdery deposits
Stage 3: sufficient corrosion losses resulting in degraded strength of base material
Stage 4: severe corrosion resulting in perforation of material

5.3.3   Forms of Corrosion Observed

The primary forms of corrosion exhibited on ground vehicles include uniform corrosion, crevice and poultice corrosion, galvanic corrosion and pitting. If however, there may be other forms of corrosion that appear on vehicles. In the following sections, some of these forms of corrosion are described briefly as they pertain to ground vehicles.

5.3.3.1 Uniform Corrosion

Although it may not be the most damaging form of corrosion, uniform corrosion is the most common form found on ground vehicles and automobiles. Corrosion in this form is usually more degrading to appearance than the structural integrity of the vehicle.

5.3.3.2 Crevice Corrosion

Crevice corrosion commonly occurs on military ground vehicles, especially when metal plates or other "post-production" components are bolted or welded onto the vehicle. This allows moisture to seep in and become trapped, ultimately corroding the metal. Often, there are other pre-existing areas that are susceptible to crevice corrosion, for example, holes, joints and under fasteners. Electrical connectors also have a tendency to corrode by crevice corrosion.

5.3.3.3 Poultice Corrosion

Poultice corrosion is a form of crevice corrosion that occurs as a result of mud, salt, and other road debris getting deposited on the wheel wells, underside, and other locations on the vehicle. A simple way to mitigate poultice corrosion that may occur from road debris is to frequently wash off the deposits, especially on the underside of the vehicle. Absorbent materials such as wood, cardboard, open-cell foams and sponge rubber can cause poultice corrosion to occur, since they can attract moisture. To avoid poultice corrosion caused by such materials, they should not be in contact with metals.

5.3.3.4 Galvanic Corrosion

Since the framework of most ground vehicles is made from steel, galvanic corrosion is a major concern if different metals such as aluminum are used for other components. Any such use of different metals should be electrically isolated from each other.

5.3.3.5 Pitting Corrosion

Pitting will often occur on parts of a vehicle that have damaged coatings. The discontinuity in the protective coating exposes a localized area to the corrosive environment the vehicle is in. For example, if the vehicle is being operated in a location near the ocean, chlorides will attack the damaged area.

5.3.3.6 Erosion Corrosion

Erosion corrosion may occur on amphibious vehicles that use propellers for propulsion in water, such as the AAV, EFV, and the Light Armored Vehicles. For more information on erosion corrosion, see Section 5.1.3.11.

5.3.3.7 High Temperature Corrosion

There are a number of components that may experience high temperature corrosion, including those used in the engine and exhaust systems. The very high temperatures set up the conditions for a rapidly corrosive environment experienced in these applications.

5.3.4   Types of Metals used in Vehicles

Much less consideration is given to minimizing weight when selecting materials to be used on land vehicles than it is for aircraft. Therefore, steel is the primary material chosen for many components, since it provides good mechanical properties and is relatively inexpensive. This choice, however, leads to a number of corrosion problems. Aluminum alloys are also typically used to construct certain ground vehicle components.

5.3.4.1   Steel

A large percentage of major components on wheeled ground vehicles are constructed from mild and stainless steels. For example the exhaust system on the HMMWV is comprised of a 409 stainless steel muffler with mild steel brackets and flanges, and the inlet pipe and heat shield are both made of aluminized steel.[60]   Frame rails and cross members on the HMMWV are also composed of mild steel. Other examples of areas that are made of steel are given in Table 55.

Table 55   Examples of Wheeled-Vehicle Steel Components[60]

Vehicle Component	HMMWV	M939 5-Ton Truck
Head Lamp		
Outside Ring	Steel	Steel
Lens Retainer	Zinc plated steel	Zinc plated steel
Main Housing	Steel	Steel
Fuel and Brake Lines		
Fuel Tank Supply Lines	Steel with Pb-Sn hot dip	
Rear Brake Lines	Cu-brazed steel with Pb-Sn hot dip	
Front Brake Lines	Cu-brazed steel with Pb-Sn hot dip	
Exhaust System		
Muffler	409 stainless steel	Aluminized steel
Fording Kit	Steel	
Valve Cover	Steel	
Vehicle Body		
Hard Top Latch	Steel	Steel
Rear Corner Panels	Steel	Steel
Door Frames	Steel	Steel
Door Posts	Steel	Steel
Roof Gutters	Steel	Steel

Steel, especially mild steel, is very susceptible to a number of forms of attack in many different environments. Therefore, it is very important that corrosion protection and control methods are used to protect steel components from corroding. Alternatively, new corrosion resistant materials should be used in place of steel wherever possible.

5.3.4.2   Aluminum

Aluminum has been used for electrical connectors on land vehicle systems, and is susceptible to crevice corrosion. It has also been used for non-armor body panels.

The hull of the AAV is fabricated from aluminum alloy 5083, which is susceptible to galvanic and crevice corrosion. Aluminum alloy 2519-T87 is the primary structural alloy used for the hull on the EFV, but is relatively susceptible to corrosion, typically in the form of pitting induced by galvanic effects between the aluminum and steel fasteners. Therefore, corrosion protective coatings must be used. The 5083 aluminum alloy is generally less susceptible to corrosion compared to aluminum alloy 2519, especially galvanic corrosion from steel bolt fasteners. Both alloys are used as hull materials but also serve as integral armor for the amphibious vehicles.[61]

5.3.5   Corrosion Prevention and Control – Methods and Maintenance

Proper corrosion prevention and control methods are necessary to maintain ground vehicles in good operating condition with minimal maintenance. Coatings, material selection and design are three ways to significantly reduce the impact of corrosion, if they are performed appropriately.

5.3.5.1   Coatings and Surface Treatments

Applying protective coatings is possibly the most widespread method of corrosion protection used for ground vehicles. Steel body panels must be protected in order to provide a strong resistance to corrosion. Applying a zinc coating (galvanized steel) is a common way to improve corrosion resistance. (Aluminum coatings are also used as a sacrificial coating.) The common methods of application are hot-dipping and electrogalvanizing. Coatings are typically applied over the galvanized components to provide a barrier to the corrosive environments as well as an aesthetic appearance.

An important consideration when choosing coatings to protect ground vehicles from corrosion is the abrasion resistance. Ground vehicles operate in various environments, but they also may be subjected to driving through underbrush and other conditions that may be abrasive to the surface. Damaged coatings can lead to an acceleration of localized corrosion.

Conversion coatings can be used to prepare the surface of a corroded surface (after the corrosion products have been properly removed) so that a topcoat can be applied to seal a creviced area or provide additional corrosion resistance. They can also be applied as a stand-alone method to provide enhanced corrosion resistance.

Since crevice corrosion is especially a problem in ground vehicles, it is very important to keep tight areas and crevices sealed from the external environment. CPCs are used, often to displace any water that would otherwise get trapped in such crevices. Thin-film coatings also act as a barrier to prevent moisture and salt from attacking a surface, and are very good for reducing corrosion in crevice areas.

5.3.5.2   Maintenance

Regular washing of ground vehicles can significantly reduce the rate of corrosion. It is even more important when the vehicles are exposed to marine or industrial environments, or deicing agents from roadways, since the chlorides and other harmful agents buildup on metal surfaces.

Climate controlled storage can also significantly reduce the rate of corrosion. That is, storing vehicles in a controlled atmosphere with low relative humidity will virtually eliminate corrosion.

5.3.5.3   Design and Material Selection

Avoiding structures that can trap moisture or other corrosive media is a key to effectively designing in corrosion resistance to a vehicle. For instance, butt joints instead of lap joints lessens the crevices available to trap moisture. Using welded joints instead of bolts or rivets, in particular, can typically help to reduce the crevices available for corrosion to occur. Welding, however, may also increase the available crevices if the welds are discontinuous or incomplete. This method of eliminating crevices, as well as incorporating drain holes and providing proper sealing of crevices are good examples of design procedures to improve the inherent corrosion resistance of a vehicle. As with any application proper, selection of the material to be used for a component can significantly increase the corrosion resistance of the system.

5.4   Structures

It is beyond the scope of this book to cover all types of structures and their susceptibility to corrosive environments and forms of attack. Instead some of the common building blocks and more important structures are touched upon in this section. More importantly, the typical metals used, typical corrosive environments encountered, as well as some of the forms of corrosion and corrosion prevention methods are discussed briefly.

5.4.1   Typical Corrosive Environments

Unlike vehicles, structures are generally immobile and confined to one location. Therefore, it is relatively easier to determine the corrosive environments and the forms of attack the structures will have to endure. Most structures, for example, are primarily subject to the atmospheric environment and climate (e.g. weather). In addition to the atmospheric environment, some structures and structural elements must endure more extreme conditions such as direct contact with pollution (e.g. smoke stacks) or the marine environment (e.g. bridges and piers). Moreover, some structures and structural elements have a functional role in a process, such as pipelines, storage containers and chemical reactors. Pipelines carry fluids, such as water or crude oil, which can be very corrosive; storage containers hold fluids that may be corrosive; and reactors are often subject to extreme conditions, such as strong acids/bases, organic compounds, solvents, and high temperatures and pressures.

Structures residing in rural locations with dry climates typically experience the slowest rate of atmospheric corrosion, while those in industrial or marine environments usually experience a much higher rate. Some structures are buried underground, including storage tanks and pipelines. Therefore, these must be resistant to the particular soil environment, which may contain contaminants, as well as ground water. Contaminants and ground water together can create a very corrosive environment.

5.4.2 Structures Typically Susceptible to Corrosion

Typically the types of structures addressed in this section are referred to as infrastructure, such as bridges, buildings, and larger pieces of equipment such as storage tanks, processing equipment and reactors. The corrosion of pipelines is a significant problem, as shown in Figure 52.

Figure 52   Corrosion on High Temperature Pipelines at an Air Force Facility[42]

5.4.3 Forms of Corrosion Observed

5.4.3.1   Uniform Corrosion

Uniform or general corrosion is commonly observed on structures and structural elements since they typically have large areas exposed to the atmosphere. Furthermore, most structures are built using steel, and since steel typically corrodes in a more uniform fashion, general corrosion is especially evident. Although it greatly degrades the appearance of the structure, uniform corrosion does not usually diminish its structural integrity, at least not initially. However, left untreated for long periods of time (depending on the corrosive environmental conditions) the structure may eventually fail due to corrosion, especially if it is supporting a significant load.

5.4.3.2   Pitting Corrosion

Localized corrosion such as pitting may also be found on structures. This form of corrosion may be less common than uniform corrosion on structures, but can have more severe consequences. Since pitting can perforate a metal much more rapidly than uniform corrosion, the structure or structural element can experience a mechanical failure in far less time. Pitting tends to occur when there are more corrosive agents or contaminants present in the atmosphere or environment. Industrial environments containing hydrogen sulfide pollutants, for example, can rapidly attack structures in the form of pitting. In addition, the marine atmosphere, which contains a high

concentration of chlorides, may have a similar effect. In storage containers and reactors pitting may occur where the protective lining/coating has broken down or has been damaged.

5.4.3.3   Stress Corrosion Cracking

Stress corrosion cracking is a significant concern with regard to structures and structural elements since by definition they provide support against loads. Stress corrosion cracking can result when structural loading is combined with a corrosive environment, and therefore structures are inherently susceptible to SCC. Since this is widely known to be a concern, metals resistant to cracking and SCC are most often used in structures, especially those that must support significant loads. In the case where the loads may not be as significant, SCC remains a concern and proper material selection should be performed in order to avoid a catastrophic failure of the structure. SCC is also a serious consideration in storage tanks and reactors since their interiors may be exposed to extremely corrosive conditions, while supporting the structural load.

5.4.3.4   Galvanic Corrosion

Galvanic corrosion is usually less of a concern in structures for a few different reasons. First, it is common to use the same or similar metals in the structure, and in most cases the metal used is steel. When the metals are not exactly the same, they are typically very similar, for example, different grades of steel. Therefore, without having significantly different metals, galvanic corrosion does not usually take place to any noticeable extent.

Secondly, structures usually have a very large area, in which case the area effects that take place in galvanic corrosion favor the structure. For instance, in the case of a small metal component that is attached to and dissimilar to the structure, the structure will not be affected to any significant extent. Even if the structure is anodic compared to the metal component, the amount of corrosion will be small if the area ratio is large. Galvanic corrosion, however, can have a significant effect on the smaller metal component if it is the anode. For example, fasteners used to join large steel components will corrode rapidly in a corrosive environment due to galvanic action if they are more anodic to the steel. Therefore, the fasteners should either be made of a similar metal or they should have a corrosion protecting coating.

5.4.3.5   Crevice Corrosion

Crevice corrosion occurs in structures where there are tight areas which allow for moisture ingress. Leaks from piping systems or fluid handling systems can lead to crevice corrosion, if the moisture becomes trapped or stagnant in the structure. Storage tanks and reactors are especially susceptible to crevice corrosion, if their sealants or gaskets deteriorate over time and allow moisture or corrosive fluid to become trapped.

Furthermore, materials that absorb and hold moisture may also lead to crevice corrosion in structures. The ingress of moisture in steel reinforced concrete has been a known problem which leads to the corrosion of the steel reinforcements. This is especially the case in locations near seawater where chlorides are present in the atmosphere. These chlorides may accelerate the rate of corrosion in structures.

5.4.3.6   Erosion Corrosion

The only structures that typically experience erosion corrosion to a significant extent are those that are exposed to a flowing fluid. Bridge and pier columns, for example, are partially immersed in water and therefore are subject to erosion corrosion. Columns immersed in seawater experience perhaps one of the most severely corrosive environments since the waves and sea spray erodes and corrodes the structure. This severe environment occurs in seawater in the area just above the water line, called the splash zone. This can lead to a rapid degradation of the structure causing a significant amount of damage. Therefore, materials that are resistant to erosion corrosion should be used in these types of applications.

5.4.4   Types of Metals Used in Structures

Structural elements are almost entirely made from low to medium carbon steels and steel reinforced concrete. The driving factors for their selection have been their mechanical properties, cost, and manufacturability including excellent welding characteristics of the carbon steels. The strategy has been to use the low cost materials and then employ corrosion protective technologies to limit corrosive attack. This has led to high maintenance costs in areas where the corrosion protection schemes have quickly degraded exposing the steel to attack. The selection of materials for structural elements is highly dependent upon the corrosivity of the environment and the design of structural elements. For the containers and reactors that handle corrosive fluids, the interior usually has a protective liner or coating that is compatible with the fluid and conditions they are subjected to.

5.4.4.1   Carbon Steels

The atmospheric and chemical corrosion of carbon steels will be addressed in a later section but other issues surrounding the vulnerability of structural carbon steels will be discussed here. Carbon steels can be used effectively as structural elements lasting many years in non-corrosive environments if the proper alloy selection and protection methods are used. However, due to the general susceptibility of carbon steels to numerous forms of corrosion, high maintenance can be expected in corrosive environments.

Carbon steels have been used successfully for structures exposed to the outdoor elements in non-marine type atmospheres. The steels are usually alloyed with small amounts of Cr, Ni, and Cu creating a class of steels referred to as weathering steels. These steels will corrode rapidly when first exposed to the atmosphere creating an oxide scale layer which significantly reduces the rate of corrosion thereafter. Weathering steels have been used, uncoated, for inland structures such as bridges. In marine environments, coatings must be used to provide the highest level of protection against corrosion.

5.4.4.2   Steel Reinforced Concrete

Steel reinforced concrete is another widely used material for structures including buildings, bridges, and dams. Normally, one would expect that the concrete provides corrosion protection of the reinforced steel rebar found within the concrete. However, the corrosion of rebar and the consequential degradation of concrete is a significant problem that afflicts a large portion of infrastructure.

Steel naturally tends to form a passive oxide film when it is exposed to the atmosphere. This film provides protection of the steel from corrosion, and when new, hydrated concrete surrounds the rebar it acts to preserve the steel from corroding further by creating an environment with a high alkalinity. This alkaline environment, which includes calcium hydroxide, potassium hydroxide, and sodium hydroxide, typically has a pH of approximately 12.5, and in the presence of oxygen it helps to maintain the passive oxide layer.[62, 63] However, concrete is permeable to carbonation and chlorides, which will degrade the protective oxide layer on steel and readily corrode the rebar.

Once the concrete has dried around the rebar, the residual structure has a degree of porosity that allows atmospheric molecules and ions to diffuse through the concrete. Carbon dioxide, which is readily available from the atmosphere, can then permeate the concrete. The carbon dioxide reacts with the hydroxides to produce carbonates such as calcium carbonate, resulting in the environment having a significantly lower pH of approximately 8 or 9. Consequently, the passive oxide film protecting the steel can no longer be maintained and corrosion of the steel resumes. The rate of diffusion of the carbon dioxide is directly dependent on the porosity and permeability of the concrete structure. Therefore, higher quality concrete with a low porosity is very likely to reduce the rate of corrosion of the reinforcing steel compared to concrete with a higher porosity.[63]

Of course, once the oxide film protection of the steel rebar is degraded, the steel becomes much more susceptible to corrosive attack. This is especially a problem in humid and marine environments which can accelerate the rate of corrosion. Chloride ions are the primary threat to steel rebar, and are obviously present in marine environments, but can also be present in non-marine environments, such as locations where rock salt is used to melt snow and ice. There only needs to be a minimal amount of chloride ions present to induce corrosion of the rebar. For instance, the minimum amount for reinforced concrete in wet conditions is only 0.10% chloride by weight and 0.20% in dry conditions. Since the distribution of chloride ions at the steel rebar surface is not usually even, the breakdown of the oxide film also occurs in a non uniform fashion. Consequently, galvanic effects will begin to take place because part of the rebar, where the oxide film has not been degraded, is still in a passive (cathodic) state and another part is in an active (anodic) state. Furthermore, much of the rebar structure is physically connected providing an electrical path for any induced corrosion currents to follow. Localized galvanic effects may also be induced by differences in grain structure of the steel.[63]

As a result of the corrosion of the steel, corrosion products are deposited on the surface of the rebar, which leads to a volumetric expansion, and the steel then occupies a greater amount of space than the original rebar. Since concrete does not perform well in tension, the expansion causes the weak concrete structure to fracture and in the worst case even spall. The aftermath of this corrosion process including spall is illustrated in Figure 53 where a couple of steel reinforced concrete pier support columns have shown severe degradation due to the corrosion of steel reinforcements in a marine environment.
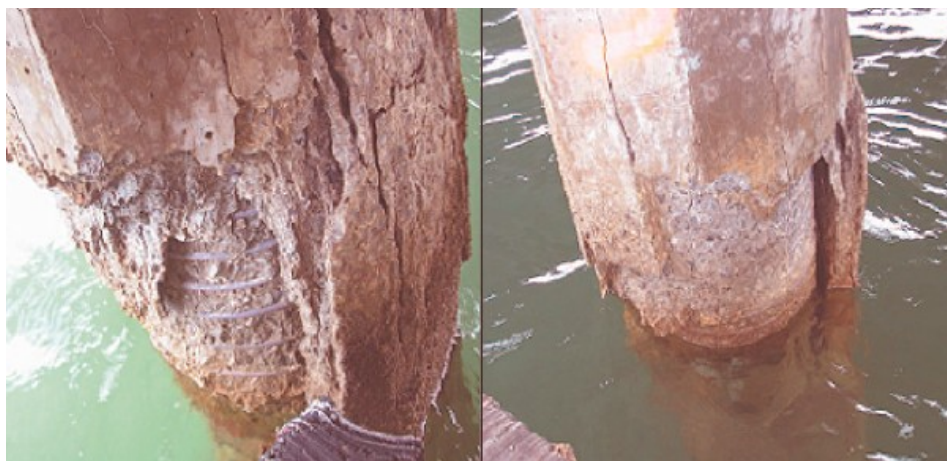
Figure 53   Corrosion and Degradation of Steel Reinforced Concrete Bridge Columns in Seawater at a Naval Station[42]

The fractured or spalled concrete structure then allows even more penetration of corrosive agents, including moisture and chlorides. This of course can lead to a sharply increasing rate of corrosion and degradation of the reinforced concrete structure. When corrosion of the steel rebar occurs leading to spall, the reinforced concrete structure is significantly weakened and may be subject to collapse under compressive loads if it is not attended to and repaired.[63]

Initially, methods to reduce carbon dioxide and corrosive agents from reaching the rebar included placing them sufficiently deep in the concrete, ≥ 2 inches, and using low water content when producing concrete to lower its permeability. These methods, however, were found to be inadequate in significantly reducing corrosion due to chlorides. Additional methods introduced to deter corrosion included coated rebar and cathodic protection of uncoated rebar. Epoxy systems have been found to provide the best protection against chlorides. The epoxies have low bond strengths making the coating process crucial to providing the best protection. Epoxy coatings are generally deposited using electrostatic powder spray and baked to fuse the epoxy. An adequate thickness must be produced of about 0.18 ± 0.05 mm. Zinc coatings have been found to provide good protection against carbonates, but are susceptible to chlorides. More recently, stainless steel rebar has been used for reinforcing concrete taking the place of the traditional rebar steel.

5.4.5   Corrosion Prevention and Control – Methods and Maintenance

There are often corrosion protection methods employed to inhibit the corrosion of structures. These include all of the traditional methods, such as coatings and sealants, as well as cathodic protection and inhibitors. Proper design, material selection, and maintenance are also very important in order to reduce the corrosion of metals in structures over time and to increase their lifetime.

5.4.5.1   Coatings

Coatings are commonly used in order to protect structures from corrosion, including organic and inorganic coatings as well as sealants. It is important, however, to repair any damaged coatings as they may exhibit in increased rate of corrosive attack.

Organic coatings are the most widely used for carbon steel protection applicable to bulk structures. For example, alkyd coatings (a specific type of polyester resin) are useful for protection of steel structures that are exposed to a relatively dry, nonchemical, atmospheric environment. They are not resistant to immersion in any type of water environment, chemical environments (acid or alkali), nor are they resistant to highly humid environments. Alkyds are generally incompatible with alkaline (e.g. galvanized) surfaces, concrete, mortar and most cementitious surfaces. They are commonly used for outdoor steel structures such as the exterior of buildings, handrails, cranes, and gantries. Their widespread use is partially attributable to their ease of application, relative low cost, weathering properties, and ability to adhere to poorly prepared or dirty surfaces. These alkyd coatings can be modified with phenolic, vinyl, silicone, epoxy, or urethane to improve various properties including appearance, water resistance, alkali resistance, adhesion, solvent resistance, thermal resistance, chemical resistance, and durability. For example, silicone-modified alkyd coatings are used extensively in marine environments due to a greatly improved moisture resistance.[64]

Hot-melted coal tar coatings are used on underground and water-immersed pipelines because they have exhibited excellent protection properties in these environments. For industrial protection, epoxy resin coatings are the most common types used. Amine-cured epoxies are often used as protective liners in steel and concrete tanks to provide corrosion protection from water or aqueous chemicals. Polyamide epoxy coatings are commonly used in high humidity environments and to protect steel in fresh and seawater conditions. Vinyl acetate copolymer coatings also are used to protect steel from corrosion in submerged environments, such as in locks and dams. Vinyl butyral primers are excellent for the corrosion protection of steel, aluminum, magnesium, and other metals in submerged seawater and freshwater environments.[64]

Inorganic coatings provide the best resistance to solvents and find uses in chemical plants, petroleum refineries, and other facilities where chemical vapors are present. Thermally sprayed zinc and aluminum (and their alloys) coatings provide excellent protection in marine and industrial environments. Metal coatings find applications for small scale structural elements such as fasteners. Zinc coatings are the most popular for carbon steels and are applied by either hot-dip galvanizing or electroplating.

5.4.5.2   Cathodic Protection

Another method employed to protect structures from corrosion is the use of cathodic protection by impressed current or sacrificial anodes. The placement of sacrificial anodes on vulnerable areas of a structure may improve that structures resistance to corrosion. In the same way, impressed current cathodic protection (method of supplying electrons from an external power source to prevent corrosion reactions occurring on the metal) is used to protect structures. For example, impressed current cathodic protection is often used on pipelines in order to reduce the rate of oxidation occurring on the surface of the pipeline.

5.4.5.3   Design, Material Selection, and Maintenance

The design of structures also has an effect on the corrosion characteristics. The strategies in providing structural designs that limit corrosive attack include the following:

- avoid upturned angles and channels which collect liquids and solids
- use welds instead of fasteners wherever possible (limit crevices)
- grind welds flush with surface of metal

Proper design includes the elimination or sealing of any crevices that can trap moisture. Also, it is important that critical points in the structure are accessible for maintenance, so that proper care can be taken to prevent extensive corrosion damage. Material selection is less of an elaborate process in building structures than it is in building aircraft or ships. Even so, it is still important to select materials that are resistant to SCC, pitting as well as the other pertinent forms of corrosion. Moreover, it is important that smaller, anodic materials are not electrically connected to larger, cathodic materials in order to prevent galvanic corrosion. If small dissimilar fasteners are used, for example, they should be electrically isolated from the larger structure.

Damaged or worn coatings should be repaired in order to protect the structure from corrosion. Otherwise, if the coating is damaged and left untreated, the corrosion attack may be accelerated. Similarly, sealants and gaskets should be properly maintained or replaced if they have deteriorated. Failure to keep sealants and gaskets in good condition can lead to rapid corrosion. Spillage should also be cleaned up properly, since chemicals can actively corrode any exposed metal structure. Thus, proper maintenance is important to keep the structure protected against corrosion.

5.4.6   Corrosion Inspection and Monitoring

Corrosion inspection is a good practice to ensure the integrity of the structure is maintained. Corrosion monitoring is sometimes employed on structures that are not easily accessible for observing and inspecting for corrosion. For example, monitoring probes and devices are often installed on buried pipelines in order to observe any significant corrosion. This allows for proper maintenance of the structure before any failure may occur, and also it may eliminate unnecessary maintenance.

6.0   Corrosion Characteristics and Properties of Metals

As discussed in the previous sections, the extent and form of corrosion occurring on a metal is predominantly dictated by the environmental conditions, and thus, the interaction of the metal with the surrounding environment. Some metals are inherently resistant to the effects of corrosion, while others are inherently susceptible. This section discusses the nature of the more common types of metals and alloys in terms of their corrosion characteristics and properties. This is not a comprehensive evaluation of metals and alloys, however; these are general observations, and are not intended to provide complete guidance in materials selection. Instead, an investigation of literature should precede the selection of a material.

The corrosion characteristics and properties of metals come from field experience and extensive testing in natural, simulated, and accelerated environments. The results of testing are used to rate materials and determine what alloying and heat treatments are beneficial to corrosion resistance. Field experiences, as well as test results, are used to document susceptibilities of materials under specific conditions.   The following section uses information from both testing and field experience to facilitate the selection of metals for varying applications. The section is organized by the relative usage of the metal classes with the most widely used ferrous metals covered first.

6.1   Steels

Steels can be largely grouped into three categories with respect to corrosion resistance.[9] Carbon steels contain up to approximately 2% total alloying content with the primary additions of carbon, manganese, phosphorus and sulfur. The second group is the low alloy steels (or sometimes referred to as mild alloy steels) containing roughly 2 – 11% total alloying content. Corrosion resistance can be enhanced over carbon steels with additions of copper, nickel, chromium, silicon, and phosphorus. High corrosion resistant steels (stainless steels) can only be obtained with ≥ 11% Cr along with varying amounts of other elements.

6.1.1   Alloying for Corrosion Resistance

The primary alloying elements to increase corrosion resistance of steels are copper, chromium, silicon, phosphorus, and nickel. Broad categories of steel materials based upon alloying content include the low alloy steels, weathering steels, and stainless steels.

6.1.1.1   Carbon and Low Alloy Steels

For carbon steels, copper additions of 0.01 to 0.05% have the greatest effect for increasing general corrosion resistance, as seen in Figure 54. The relationship of the other elements on corrosion resistance is displayed in Figure 55. Small additions of chromium significantly increase tensile strength as well as increasing corrosion resistance leading to the high strength low alloy (HSLA) steels. Weathering steels is a term describing low-alloy steels with small additions of chromium, nickel, and copper. They can provide good service without any coatings in a non-marine atmospheric environment.   Many inland bridge structures make use of weathering steels.   Larger additions of chromium are required for a dramatic increase in corrosion resistance as previously mentioned.
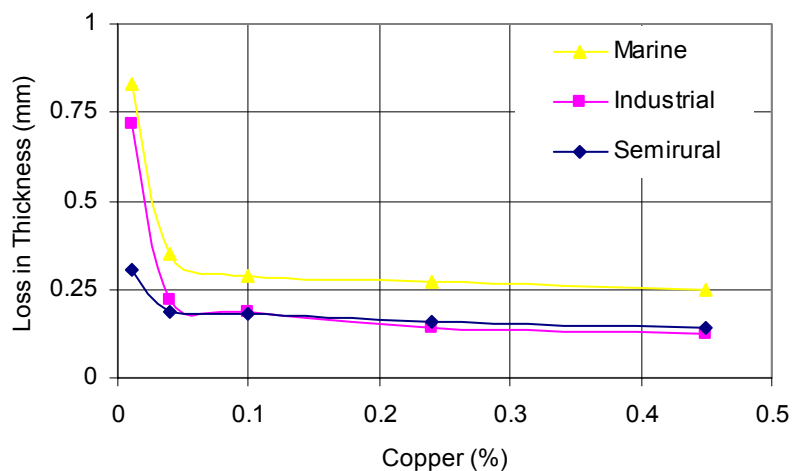
Figure 54   Effects of Copper Addition on the Uniform Atmospheric Corrosion of Steel[65]
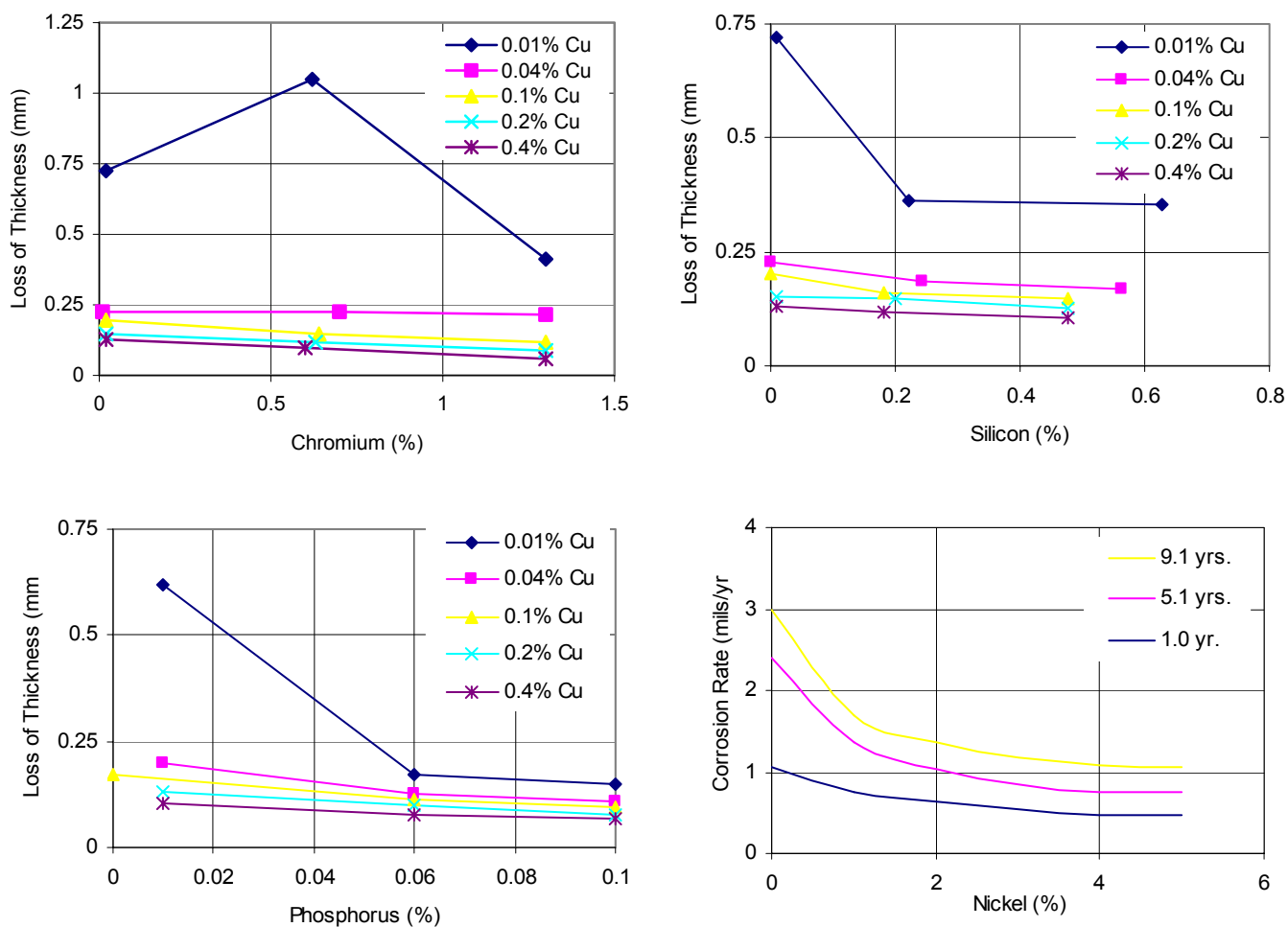
Figure 55   Effects of Alloying Elements on the Uniform Industrial Atmospheric Corrosion of Steels[65]

6.1.1.2   Stainless Steels

Stainless steels contain 11 percent or more of chromium. The higher chromium content results in the formation of a chromium oxide protective film, greatly increasing the oxidation resistance of the steel. Stainless steels are most often exposed to a passivating solution to improve formation of the protective film.[66] Corrosion resistance will generally increase with an increase in chromium content and decrease with an increase in carbon content. Stainless steels are excellent for oxidizing environments but are susceptible in halogen acids or halogen salt solutions. They are also susceptible to pitting in seawater.

6.1.1.3   Austenitic Stainless Steels

Austenitic stainless steels are the most commonly used class of stainless steels. They may be used in mild to severe corrosive environments, dependent upon alloying and are nonmagnetic compared with other steels.[66] They may be utilized in environments with temperatures reaching 600ºC and for low temperatures in the cryogenic range. Almost all austenitic stainless steels are modifications from the 18Cr – 8Ni (304) alloy. Difficulty in processing stainless steels limits increasing concentrations of chromium. The addition of nitrogen has been found to be an austenite phase stabilizer which allows higher additions of molybdenum, up to about 6%, increasing the material's corrosion resistance in chloride environments. Other additions which improve corrosion resistance to specified environments include high chromium alloys for high temperature service and high nickel alloys for inorganic acids. Table 56 represents a summary of the austenitic stainless steel alloys and their modifications in regards to corrosion resistance.

Table 56   Austenitic Stainless Steel Alloys[8]

Austenitic Stainless Steel Alloy	Aspects of Corrosion Resistance
301, 302, 303, 303Se, 304, 304L, 304N	No significant change in general corrosion resistance between these grades. 304, including 304L and 304N, slightly better than the others. 303 the least resistant with a greater susceptibility to pitting.
302B	Modified 302 with 2.5% Si resulting in increased oxidation resistance at elevated temperatures.
321, 347, 348	Generally the same corrosion resistance as the above alloys, with the added benefit of near immunity to heat sensitization. They have been stabilized with the addition of titanium and/or niobium.
305, 384	Higher nickel contents result in higher corrosion resistance.
308, 309, 309S, 310, 310S	All are higher in chromium and nickel content resulting in increased corrosion resistance and oxidation at elevated temperatures.
314	Similar to 310 but with silicon addition for better resistance especially to sulfuric acid.
316, 316L, 316F, 316N, 317, 317L	Same general corrosion resistance as 310 but with an increase in localized corrosion resistance, especially pitting.

6.1.1.4   Ferritic Stainless Steels

Ferritic stainless steels generally do not match the corrosion resistance of the austenitic grades. They exhibit relatively high yield strength and a low ductility and are magnetic. The ferrites have a low solubility for some elements such as carbon and nitrogen. The ferritic stainless steels will transition from ductile to brittle over a small temperature range, occurring above ambient temperature for increasing carbon and nitrogen content and more so with increased chromium content. Ferritic alloys have been developed using an argon-oxygen decarburization (AOD) process, significantly reducing carbon and nitrogen levels. Also, reactive elements such as titanium and niobium may be added to precipitate some of the carbon and nitrogen. Ferritic stainless steel alloys containing carbon and nitrogen are susceptible to intergranular corrosion by heat sensitization through heat treating, welding, or other thermal exposure. Newer alloys, such as 444, have lower carbon and nitrogen content, using AOD, allowing higher chromium and molybdenum content resulting in an alloy more amenable to welding and somewhat tougher, although still limited by a lack of toughness. Ferritic stainless steels do offer use in thermal transfer applications as a result of their high resistance to SCC in chloride environments. The 409 alloy was specifically developed for use in automotive exhaust components. Table 57 lists the ferritic alloys with their corrosion characteristics.

Table 57   Ferritic Stainless Steel Alloys[8]

Ferritic Stainless Steel Alloy	Aspects of Corrosion Resistance
405	12.5% Cr, ≤ 0.08% C, 0.10 to 0.30 Al Low corrosion resistance, ideal for welding, used principally as a lining for pressure vessels
409	10.5 to 11.75% Cr, stabilized with Ti. Lowest corrosion resistance of all stainless steels
429	Contains 14.0 to 16.0% Cr and some carbon Developed for a higher degree of weldability than 430
430, 430F, 430FSe, 434, 436	17% Cr , high atmospheric corrosion resistance and resistance to many chemicals. 430F has reduced corrosion resistance with increased machinability 434 has 1.0% Mo for pitting resistance 436 has 1.0% Mo plus up to 0.7% Nb and Ta for carbide stabilization. Better for elevated temperature service.
442, 446	18.0 to 23.0% Cr for 442 and 23.0 to 27.0% Cr for 446 No appreciable increase in corrosion resistance, used in heat processing equipment as they have a high resistance to scaling through high temperatures.

6.1.1.5   Martensitic Stainless Steels

Martensitic stainless steels have a much lower corrosion resistance than austenitic grades, and usually slightly lower than the ferritic grades. The martensitic stainless steels contain lower Cr and higher C concentrations compared with the other stainless steels. This structure results in a strong but brittle class of materials. They may be tempered to improve toughness, but to limited degree. Additions of nitrogen, nickel, and molybdenum at lower levels of carbon have been

found to produce alloys with better toughness and corrosion resistance properties. The corrosion characteristics of the martensitic grades are summarized in Table 58.

Table 58   Martensitic Stainless Steel Alloys[8]

Martensitic Stainless Steel Alloy	Aspects of Corrosion Resistance
403,410	Contain about 12.5% Cr with no other alloying elements
416, 416Se	Contain about 12.5% Cr with additives to improve machinability that results in somewhat less corrosion resistance.
414, 431	Both have nickel additions of about 2%. 414 is a 12-2 alloy and 431 is a 16-2 alloy. They have a higher corrosion resistance than the other martensitic stainless steels with 431 considered the highest corrosion resistance.
420, 420F	Contain higher Cr content but with no appreciable gain in corrosion resistance over 410. 420F has sulfur addition for machinability resulting in a slight sacrifice in corrosion resistance.
422	A 12.5% Cr alloy with additions to improve high temperature service.
440A, 440B, 440C	Higher Cr content and high carbon content. Lowest corrosion resistance of the martensitic due to the carbon.

6.1.1.6   Precipitation Hardening Stainless Steels

Precipitation-hardening (PH) stainless steels are Cr-Ni alloys that are hardened at moderately high temperatures, by adding elements such as copper and/or aluminum which form intermetallic precipitates. PH stainless steels may have austenitic, semi-austenitic, or martensitic structures. They must not be further exposed to elevated temperatures, once hardened, as the precipitates will be altered, degrading the material's strength. This includes welding and environmental exposures. The corrosion aspects of the PH stainless steels are presented in Table 59.

Table 59   Precipitation-Hardened Stainless Steel Alloys[8]

Precipitation-Hardened Stainless Steel Alloy	Aspects of Corrosion Resistance
630	Copper addition is used as the hardening agent. Has a martensitic structure with corrosion characteristics similar to 304 austenitic stainless steels.
631	Has a duplex structure in the heat treated condition. Exhibits a high strength with good corrosion resistance.
632	Similar to 630 but with molybdenum addition which improves strength and resistance to pitting.
633	Has a duplex structure and a higher alloying content than the other PH stainless steels resulting in increased resistance.
634	Has a semi-austenitic structure with molybdenum addition for pitting resistance.

6.1.1.7   Duplex Stainless Steels

Duplex stainless steels are two phase materials containing roughly equal amounts of ferrite and austenite phases developed specifically as a high corrosion resistant material. They contain high levels of chromium (20 – 30%), Ni (5 – 10%), and low carbon content (< 0.03%). They may additionally contain molybdenum, nitrogen, tungsten, and copper as modifiers to increase corrosion resistance in specific environments. Duplex stainless steels offer strength about double that of austenitic stainless steels, with increased resistance to chloride induced SCC and pitting. They are typically used in temperatures ranging from -60 to 300ºC. There are four primary alloys of duplex stainless steels used which are:

2304: Fe – 23Cr – 4N – 0.1N

2205: Fe – 22Cr – 5.5Ni – 3Mo – 0.15N

2505: Fe – 25Cr – 5Ni – 2.5Mo – 0.17N - Cu

2507: Fe – 25Cr – 7Ni – 3.5Mo – 0.25N – W – Cu

Increasing Corrosion Resistance

Duplex stainless steels have been used extensively in oil and gas production equipment having excellent resistance to the corrosive byproducts. They have also replaced other stainless steels that had corrosion problems in chemically corrosive environments and in heat transfer equipment due to their better resistance to SCC.

6.1.1.8   Iron-based Superalloys

Iron-based superalloys are also an extension of the stainless steels. They contain 20 – 30% chromium plus other alloying elements. They offer good corrosion resistance in a service temperature higher than the duplex stainless steels, but lower than nickel-based superalloys (up to about 815ºC). The cost of the iron-based superalloys is lower than nickel-based superalloys making them marketable in this service temperature range. Iron-based superalloys are used in structural components for furnaces, in steam and gas turbines, and in chemical processing equipment.

6.1.2   Resistance to Forms of Corrosion

The resistance of steels to corrosion varies greatly with alloying content playing a major role. Carbon and low alloy steels have the second highest uniform corrosion rates of any metals, while high alloyed stainless steels are generally only susceptible to localized corrosion. The following sections highlight the susceptibilities of steels to forms of corrosion.

6.1.2.1   Uniform Corrosion

Carbon and low alloy steels are susceptible to uniform atmospheric corrosion while stainless steels are considered resistant. Figure 56 summarizes data collected on various carbon and low alloy steels tested for uniform corrosion in a natural atmospheric environment. The graphs clearly show the decline in corrosion rate over time, with the exception of the severe marine environment.
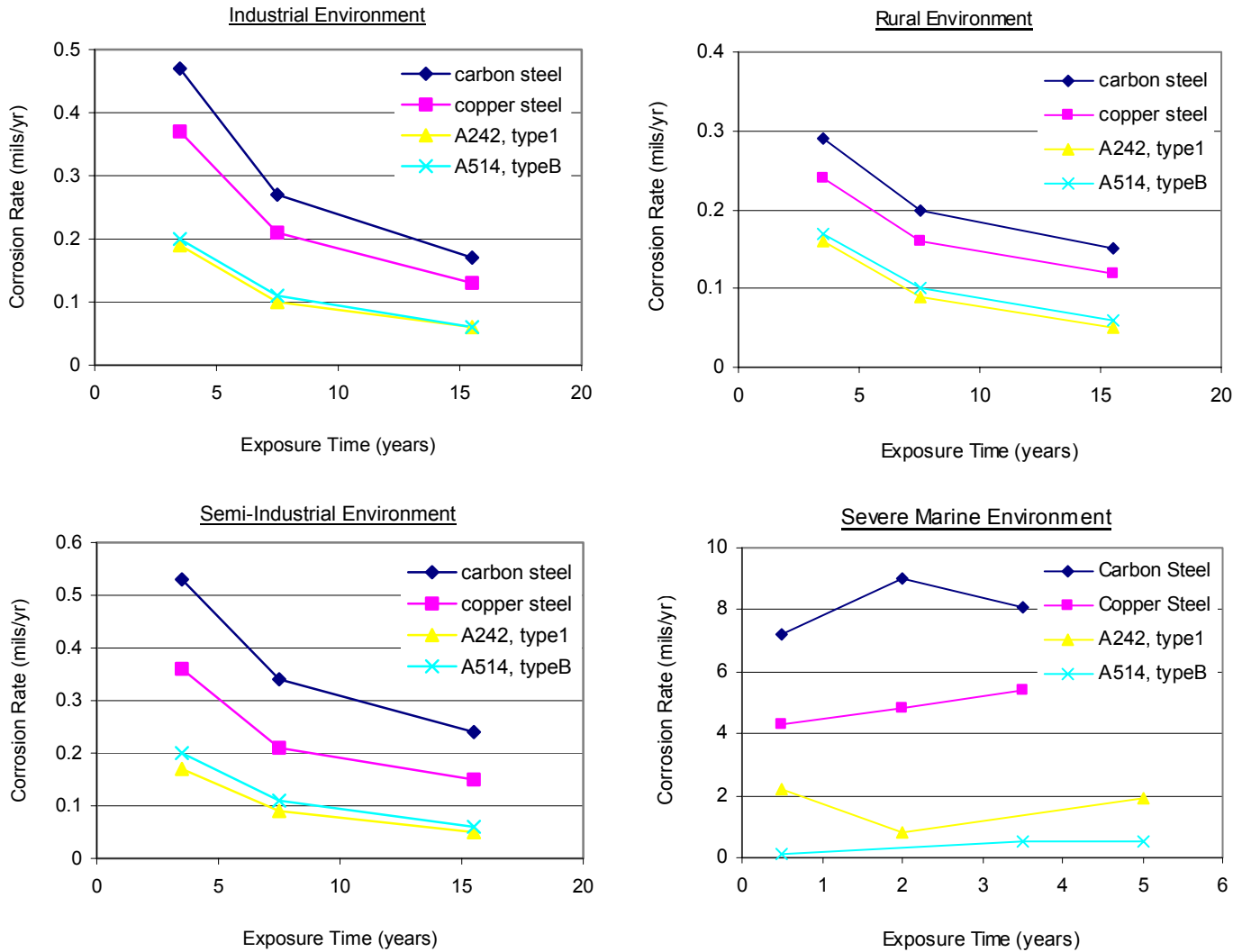
Figure 56   Uniform Corrosion of Steels in Various Atmospheric Environments

6.1.2.2   Pitting and Crevice Corrosion

Stainless steels are susceptible to pitting and crevice corrosion in marine environments, especially when fully immersed in saltwater. Stainless steels have been used on ships and can provide excellent service in marine atmospheric environments, as long as deposits are routinely washed off from surfaces. Accumulation of salt deposits will cause pitting and crevice corrosion to occur. All stainless steel alloys will exhibit pitting in low velocity seawater (less than five feet per second). Higher velocities prevent deposits and marine growth to occur so that pitting will not occur on exposed surfaces. Crevice corrosion has been found to occur, even at high velocities. The addition of molybdenum is beneficial for pitting and crevice corrosion resistance.

6.1.2.3   Stress Corrosion Cracking

Stress corrosion cracking of steels is largely a combination of their strength and environmental susceptibility. High strength steels are susceptible to SCC in corrosive environments. Failures of stainless steels in marine atmospheres have often been a result of SCC. Table 60, Table 61, and Table 62 categorize the SCC susceptibilities of steels in marine atmospheric environments.

Table 60   Steels with a High Resistance to Stress Corrosion Cracking in Atmospheric Marine Environments[67]

Materials	Type	Heat Treatment	Remarks
300 Series Stainless Steels Types 303, 304, 316, 321, 347	Austenitic	Annealing	Stressed material can crack in chloride solutions. Annealed materials are not of high strength. Cold worked materials can develop high strength, but must be stress relieved.
17-4 PH	Martensitic	H1000 and above	-
17-7 PH	Semi-austenitic	CH900	Strength is developed by cold work (60%) and aging (900ºF)
PH13-8Mo	Martensitic	H1000 and above	-
15-5 PH	Martensitic	H1000 and above	-
PH15-7Mo	Semi-austenitic	CH900	Strength is developed by cold work (60%) and aging (900ºF)
PH14-8Mo	Semi-austenitic	CH900	Strength is developed by cold work (60%) and aging (900ºF)
AM-350	Semi-austenitic	SCT1000 and above	-
AM-355	Semi-austenitic	SCT1000 and above	-
Custom-455	Semi-austenitic	H1000 and above	-
A-286	Austenitic	Solution treated and aged	
A-286	Austenitic	Cold worked and aged	Strength is developed by cold work (60%) and aging (1200ºF)

Table 60, continued - Steels with a High Resistance to Stress Corrosion Cracking in
Atmospheric Marine Environments

Materials	Type	Heat Treatment	Remarks
Inconel 718	Face centered cubic	Solution treated and aged	-
Inconel X-750	Face centered cubic	Solution treated and aged	-
Rene 41	Face centered cubic	Solution treated and aged	-
MP 35N	Face centered cubic	Solution treated and aged	Solution Annealed and cold worked (60%) and aged
Waspaloy	Face centered cubic	Solution treated and aged	-
Low-alloy steels 4130, 4140, 4340, 8740	Martensitic	Solution treated and aged	High resistance to SCC of tempered to attain strength of 160 ksi or lower.-
Maraging steel	Martensitic	Solution treated and aged	High resistance if heat treated to 200 ksi or lower.

Table 61   Steels with a High Resistance to Stress Corrosion Cracking in Atmospheric
Marine Environments if Used with Caution

Materials	Type	Heat Treatment	Remarks
Low-alloy steels 4130, 4140, 4340, 8740, D6AC, HY-TUF	Martensitic	Quenched and tempered	Good resistance to SCC if tempered to about 160 to 180 ksi.
Maraging steel	Martensitic	Solution treated and aged	All three grades; 200, 250, 300
400 series Stainless steels 410, 416, 422, 431	Martensitic	Quenched and tempered	Not susceptible if tempered at 1100°F or higher
15-5 PH	Martensitic	H950 to H1000	-
PH13-8Mo	Martensitic	H950 to H1000	-
17-4 PH	Martensitic	H950 to H1000	-
AM-355	Semi-austenitic	SCT950 to H1000	-

Table 62   Steels with a Low Resistance to Stress Corrosion Cracking in Atmospheric Marine Environments

Materials	Type	Heat Treatment	Remarks
Low-alloy steels 4130, 4140, 4340, 8740, D6AC, HY-TUF	Martensitic	Quenched and tempered	Very susceptible to SCC if tempered to attain strengths of 180 ksi and higher.
H-11	Martensitic	Quenched and tempered	-
17-7 PH	Semi-austenitic	All heat treatments except CH900	-
PH15-7Mo	Semi-austenitic	All heat treatments except CH900	-
AM-355	Semi-austenitic	Heat treatments below SCT900	-
400 series stainless steels 410, 416, 422, 431	Martensitic	Quenched and tempered	Very susceptible in the secondary hardening range, 500 to 1000ºF.

6.1.2.4   Intergranular Corrosion

Intergranular corrosion has been observed in some stainless steels primarily as a result of the precipitation of chromium carbides at grain boundaries. In austenitic stainless steels, chromium carbides are completed dissolved above temperatures of 1900ºF.[40] When slowly cooled from these temperatures, the formation of chromium carbides at grain boundaries can result. They may also be formed by reheating austenitic stainless steels into the temperature range of 800 – 1200ºF. The formation of chromium carbide precipitates at grain boundaries in ferritic stainless steels occurs for temperatures above 1700ºF. The sensitized area in welded austenitic stainless steels occurs in the heat affected zone while in ferritic stainless steels, the sensitized area is likely to be in the fusion zone and the weld itself. Methods to reduce sensitivity of stainless steels to intergranular corrosion include limiting carbon content and the addition of titanium and/or niobium which preferentially form carbides.

6.1.2.5   Hydrogen Damage in Steels

There are several different mechanisms of hydrogen attack as discussed in Section 4.9.3. Steels are susceptible to all except metal hydride formation. High strength steels are the most susceptible, although even ductile steels have been known to suffer from hydrogen damage.

6.1.3   Corrosion Resistance in Chemical Environments

Acidic environments are involved in most of the severe corrosion problems encountered with steels, as with most metals, although alkaline environments can also be responsible for increased corrosion. The corrosion rate of steels in acids depends upon the composition and concentration of acid, as well as temperature.[68] The corrosion rate of steels in hydrochloric acids will continuously increase with increasing acid concentration. In sulfuric acids, however, the corrosion rate increases until a level of concentration where passivity is reached, see Figure 57. If the passive film is damaged by mechanical or chemical means, the corrosion rate will significantly increase in concentrated solutions.
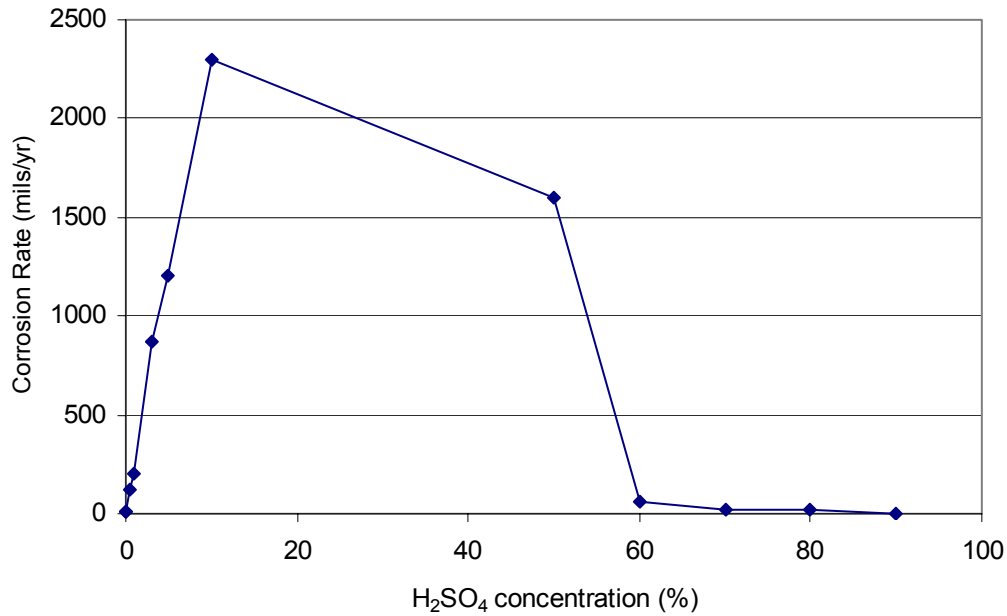
Figure 57   Uniform Corrosion of Carbon Steel by Sulfuric Acid at Room Temperature

Nitric acid readily attacks carbon and low alloy steels. Austenitic stainless steels, as well as aluminum alloys, form strong adherent oxide films. This makes them the most applicable metals for use with nitric acid.

Sodium and potassium hydroxides have similar effects on steels. The uniform corrosion rates are generally ≤ 2 mils/yr, for all concentration levels. The problem with exposure of low alloy steels to these materials is the susceptibility to SCC, sometimes referred to as caustic embrittlement. The relation of temperature and sodium hydroxide concentration to observed cracking is shown in Figure 58.

6.1.4   Corrosion Protection of Steels

Corrosion protection of carbon and low-alloy steels is almost always required. There a numerous coatings, coating processes, and methods used to limit corrosion of these steels, which include the following:[68] (Refer to Section 7.0)

- Conversion coatings
- Inhibitors
- Metal claddings
- Continuous electrodeposition
- Organic coatings (paints)
- Porcelain enameling
- Vapor-deposited coatings

- Surface modification
- Corrosion preventive compounds
- Hot-dip coating processes
- Electroplating
- Zinc-rich coatings
- Thermal spraying processes
- Pack cementation coatings

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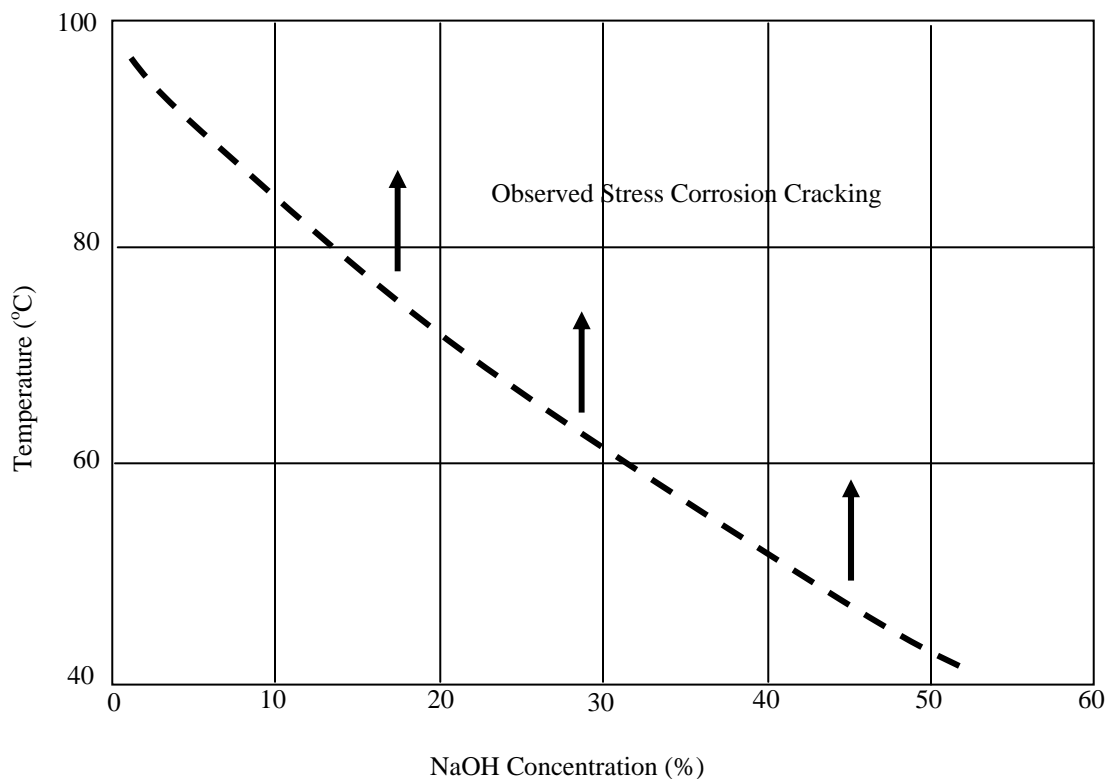
Figure 58 Susceptibility of low alloy steels to SCC in NaOH

6.2 Aluminum and Its Alloys

In general, aluminum and its alloys are more resistant to corrosion than mild steel. They are known to have a very good resistance to corrosion in a variety of environments and chemical compounds, even though aluminum is a relatively reactive metal. Aluminum and its alloys also have a good resistance to various forms of corrosive attack. For the most part, the lower temperature corrosion resistance of aluminum is virtually equivalent to that of stainless steel, and it provides reasonable protection at elevated temperatures. Pure aluminum, however, tends to have a greater corrosion resistance than its alloys, and impurities in the aluminum only act to increase the metal's susceptibility to corrosion. This is true especially for surface impurities; clean surfaces are much more effective at resisting corrosion than are surfaces with deposits.

Aluminum's excellent resistance to corrosion can usually be attributed to the rapid formation of an oxide film on the metal's surface, which acts as a barrier to corrosive environments. For instance, the film inhibits corrosion very effectively in lower temperature, atmospheric and aqueous corrosive environments. An important aspect of the film is that it forms quickly in many environments, but can also be produced artificially by sending an electric current through the metal. This is called anodizing. The tough, virtually transparent, non-flaking, aluminum oxide film is capable quickly of repairing itself when it is scratched or abraded. Therefore, in order to

defeat the protective film, continuous mechanical abrasion or chemical degradation in an oxygen deficient atmosphere is required. A further benefit is that the surface oxide film can be modified or thickened to enhance its corrosion protection.

6.2.1 Alloys and Alloying Elements

Although alloying other elements with aluminum can improve certain properties, it tends to have a negative effect on its corrosion resistance. Some elements, such as magnesium, however, can be alloyed in amounts of about <1% without significantly decreasing the corrosion resistance compared to pure aluminum. Common alloying elements include copper, magnesium, silicon, and zinc. Iron is not usually intentionally used as an alloying element, rather it is commonly a contaminant, and it is typically attributed as being the primary cause of pitting in aluminum alloys. Some of the general classes of aluminum alloys and their corrosion characteristics are described in the following sections. Although there are a number of specific aluminum alloys, only a few are discussed.

6.2.1.1 Aluminum (1000 Series)

The 1000 series of aluminum alloys has approximately 99% aluminum with the remaining percent consisting of other elements, which are considered impurities. Similar to pure aluminum, this series of metals has excellent corrosion resistance to many environments, but with increasing impurity content the corrosion resistance decreases.

6.2.1.2 Copper (2000 Series)

The 2000 series of aluminum alloys contains copper as the principal alloying element. These are higher strength alloys and are consequently used mainly for structural applications, but they have a much lower corrosion resistance compared to other aluminum alloys. Therefore, alloys with little or no copper are used for applications where corrosion resistance is important. This series of alloys, in general, is prone to stress corrosion cracking and exfoliation, and typically copper alloying results in the occurrence of uniform, pitting, and intergranular forms of corrosion to a greater extent. For instance, copper additions greater than 0.15% decreases the resistance to pitting corrosion. Alloys containing copper are also more susceptible to corrosion in seawater and marine environments.

If alloys in this series are slightly overaged, their resistance to SCC is improved to the point where the alloys are no longer susceptible to this form of corrosion. Solution heat treatment and artificial aging of 2000-series aluminum alloys, however results in $CuAl_2$ precipitates at grain boundaries, which causes the alloy to be susceptible to intergranular corrosion.[69]

Aluminum alloy 2020 in general is not suitable to be used for structural applications, but in the T651 condition it does exhibit an excellent resistance to SCC.[43, 69] Aluminum alloys 2024-T851 and 2219-T851 are also highly resistant to SCC.

6.2.1.3 Manganese (3000 Series)

Manganese is the primary alloying element in the 3000 series of aluminum alloys. These alloys exhibit a very good resistance to corrosion, in general, and are particularly very resistant to SCC.

6.2.1.4   Silicon (4000 Series)

Silicon is the main alloying element in the 4000 series of aluminum alloys, but it has little effect on the corrosion resistance of aluminum. In particular, this series of alloys is characteristically very resistant to SCC.

6.2.1.5   Magnesium and Silicon (5000 and 6000 Series)

Magnesium is the main alloying element in the 5000 series of aluminum alloys, and it provides extra protection against aqueous corrosion. Magnesium can also serve to increase the resistance to corrosion in salt water and under alkaline conditions compared to unalloyed aluminum. It may, however, also help to advance SCC and intergranular corrosion, if it is present in the grain boundaries as an anodic magnesium aluminum phase. If the magnesium content exceeds the specified limit, it tends to precipitate another phase with aluminum, and consequently causes an increase in susceptibility to intergranular corrosion. Aluminum-magnesium alloys also have a tendency to be susceptible to exfoliation.

Aluminum alloys 5083, 5086, and 5456 in the H30-series of conditions should not be used for structural applications since, they are very susceptible to SCC. Aluminum alloy 5454-H34, on the other hand, has an excellent resistance to SCC. Furthermore, the H116 and H117 tempers for the 5000-series of aluminum alloys offer a good resistance to exfoliation.

The 6000 series of aluminum alloys contain magnesium and silicon as the primary alloying elements. These alloys are stronger while maintaining the same excellent resistance to aqueous corrosion as the 5000-series alloys. However, silicon in amounts greater than 0.1% reduces the resistance to pitting corrosion, and decreases the corrosion resistance in marine environments. Furthermore, excess silicon decreases the resistance to intergranular corrosion.   Alloys containing magnesium or magnesium and silicon tend to have the best resistance to corrosion in seawater and marine environments of any of the other aluminum alloys.

In general, similar to the 5000-series, the 6000 series alloys are susceptible to SCC. In particular these alloys with >3% magnesium can be very susceptible to SCC. Cold-worked aluminum-magnesium and aluminum-magnesium-silicon alloys containing <3% Mg, however, are very resistant to SCC.[43]

6.2.1.6   Zinc (7000 Series)

Zinc is the primary alloying element in the 7000 series of aluminum alloys, and in general, as an alloying element it only has a small influence on the corrosion resistance of aluminum. These alloys, however, are characteristically much more susceptible to aqueous corrosion. A high zinc content may result in decreased resistance to intergranular corrosion, SCC, and exfoliation corrosion. In addition, zinc may decrease the resistance of aluminum to acidic environments, but may increase the resistance to alkaline environments.

Within the 7000 series of aluminum alloys, some alloys are especially susceptible to SCC and are therefore not suitable for structural applications. Overaging in the 7000 series of aluminum, however, tends to reduce their susceptibility to SCC. Aluminum alloys 7079 and 7178 are not suitable for structural applications.[43] The high strength aluminum alloy 7075 in the T6 condition is very susceptible to SCC and exfoliation, but in the T73 condition it has a greater resistance to SCC.[69] 7075 in the T7351 condition has an excellent resistance to SCC.[69] In general for the

7000-series aluminum alloys, the T76 tempers have a greater resistance to exfoliation than the T73 tempers.

6.2.1.7   Chromium

Chromium can be a beneficial alloying element because it typically provides improved corrosion resistance. For instance, Cr improves the corrosion resistance of Al-Mg and Al-Mg-Zn alloys when added in small amounts (0.1-0.3%). Furthermore, Cr increases SCC resistance in high-strength alloys, however, it does tend to increase the pitting potential in water for high purity aluminum.

6.2.1.8   Lithium

Lithium is a chemically active metal and may increase aluminum's susceptibility to corrosion. For instance, it seems that lithium additions of <3% result in a slightly more anodic aluminum.[70] This indicates that additions of lithium, however, may only increase the susceptibility of aluminum to corrosion marginally. Moreover, studies have shown that the susceptibility of the aluminum lithium alloy to corrosion is largely dependent on the δ phase, which is the AlLi phase. Increasing the amount of δ phase present, for example, increases the alloy's susceptibility to corrosion.[71]

Two of the more common aluminum lithium alloys are 2090 and 8090. 2090 is similar to 7075 aluminum in terms of resistance to SCC, and has a higher resistance to exfoliation corrosion than 7075.[70] 8090 aluminum with an altered surface structure (heat treatment T82551) has been shown to have a greater general resistance to corrosion than 2090 aluminum. Both 2090 and 8090 aluminum have been shown to be susceptible to pitting and intergranular corrosion.[71] Alloy 2097 is another aluminum lithium alloy and has shown improved pitting corrosion resistance compared to an aluminum copper alloy (2124) and comparable general corrosion resistance.[72]

6.2.1.9   Comparison of the Corrosion Resistance of Aluminum Alloys

A comparison of the relative corrosion resistance of the various groups of aluminum alloys is provided in Table 63.

6.2.2   Resistance to Forms of Corrosive Attack

Although aluminum and its alloys have a good resistance to various forms of corrosive attack, they are still susceptible to some mechanisms including galvanic, pitting, SCC, intergranular, crevice corrosion, corrosion fatigue, and occasionally filiform corrosion. Susceptibility to other forms of corrosion is often dependent on alloy composition and heat treatment.

Table 63   Comparison of the General Corrosion Resistance for the Series of Aluminum Alloys

AA Series	Principal Alloying Element(s)	Relative Corrosion Resistance
1000 Series	None	Very High
2000 Series	Copper	Low
3000 Series	Manganese	High
4000 Series	Silicon	High
5000 Series	Magnesium	Very High
6000 Series	Magnesium, Silicon	High
7000 Series	Zinc	Intermediate

6.2.2.1   Galvanic

Aluminum, especially when joined with steel, is very susceptible to galvanic corrosion. In seawater, its place on the galvanic series (see Table 19) is very low, and thus it is very anodic. It will, therefore, corrode preferentially when joined with a dissimilar metal that is higher up on the series. Graphite is very high on the galvanic series, and thus any contact with aluminum will adversely affect it in terms of corrosion. The significance of this is that graphite pencils used to make marks on aluminum may initiate corrosion by galvanic action.

6.2.2.2   Pitting

Pitting is one of the most common forms of corrosion found in aluminum and its alloys. Chloride containing environments pose one of the biggest threats to aluminum in terms of corrosion, since pitting corrosion tends to occur in salt water and marine environments. Seawater flowing at a high velocity relative to the aluminum is especially corrosive in the form of pitting since it will inhibit the protective oxide layer from automatically healing itself.

6.2.2.3   SCC

Additions of copper, magnesium and zinc in sufficient amounts can lead to SCC of aluminum alloys. SCC is dependent on the environment that the aluminum alloy is exposed to. For instance, chloride, bromide and iodide environments are particularly dangerous to aluminum since SCC tends to occur in such environments. Aluminum alloys tend to resist SCC in hydrogen, argon and air with no moisture content. Marine environments, which are commonly encountered in applications of aluminum alloys, typically promote SCC of aluminum alloys. Increasing the pH in chloride environments, however, works to inhibit SCC in aluminum and its alloys.

Furthermore, SCC can also be dependent on the heat treatment and grain orientation.[69] For example, 7075-T6 (or 2024-T4) is most susceptible to SCC when the tensile stress is applied in the short transverse direction, is less susceptible to SCC when it is applied in the long transverse direction, and is least susceptible to SCC when it is applied in the longitudinal direction.[69] (This is only the case for thick specimens; thin aluminum sheets and castings are typically not affected by this.) Shot peening can be used to improve resistance of aluminum alloy structural forgings, machined plates and extrusions to SCC and corrosion fatigue. Some environments that are

known induce or retard SCC in aluminum alloys are given in Table 64. Table 65 provides a relative comparison of various aluminum alloys and their resistance to SCC.

Table 64   Some Environments Known to Cause or Not to Cause Stress Corrosion Cracking in Aluminum Alloys[3]

	Environments Known to Cause		Environmental Additions Known to Induce or Accelerate SCC
	No SCC	SCC	
Gases	Ar (dry), He (dry), O_2 (dry), H_2 (dry), N_2 (dry), dry air	H_2O	H_2O
Liquid Metals	Li, Se, Bi, Te, Cd, Pb	Hg, Ga, Na, Te, Sn, Zn	-
Molten Salts	$AlCl_3$-LiCl, LiCl-KCl	-	-
Inorganic Liquids	H_2SO_4	H_2O	H_2O, Br^-, Cl^-, I^-
Organic Liquids	-	CCl_4, alcohols, hydrocarbons, ketones, esters	H_2O, Cl^-, Br^-, I^-

Table 65   Rating for Resistance to Stress Corrosion Cracking Aluminum Alloys in the Short Transverse Grain Direction (STGD)[43]

Alloy and Temper	Rolled Plate	Rod and Bar	Extruded Shapes	Forgings
2014-T6	Low	Low	Low	Low
2024-T3, T4	Low	Low	Low	Low
2024-T6		High		Low
2024-T8	High	Very High	High	Intermediate
2124-T851	High			
2219-T351X, T37	Very High		Very High	Very High
2219-T6	Very High	Very High	Very High	Very High
6061-T6	Very High	Very High	Very High	Very High
7005-T53, T63			Low	Low
7039-T64	Low		Low	
7049-T74	Very High		High	High
7049-T76			Intermediate	
7149-T74			High	High
7050-T74	High		High	High
7050-T76	Intermediate	High	Intermediate	
7075-T6	Low	Low	Low	Low
7075-T736				High
7075-T74	Very High	Very High	Very High	Very High
7075-T76	Intermediate		Intermediate	
7175-T736			High	
7475-T6	Low			
7475-T73	Very High			
7475-T76	Intermediate			

6.2.2.4   Intergranular Corrosion

Inhomogeneities in the alloy structure are commonly the cause of intergranular corrosion in aluminum alloys. Furthermore, alloys with a high copper content tend to be susceptible to intergranular corrosion.

6.2.2.5   Crevice Corrosion and Exfoliation

Aluminum is also susceptible to crevice corrosion, and since it is often used in components where joining and fastening is required, crevices must be eliminated to avoid this particular form of corrosion. Exfoliation in aluminum is commonly a consequence of crevice or galvanic corrosion. Aluminum alloys that have elongated grain structures are susceptible to exfoliation.

6.2.3   Corrosion Resistance in Various Environments

Periodic cleansing (e.g. rain) of aluminum and aluminum alloys can extend their life significantly in terms of corrosion resistance. This is especially true if the metals are exposed to environments with high salt content or other air contaminants, such as in marine and industrial locations, respectively. Furthermore, aluminum should not be stored in humid environments unless coated with a corrosion inhibitor.

6.2.3.1   Water

Aluminum is strongly resistant to corrosion in normal atmospheric environments, fresh water environments, distilled water environments and other aqueous environments. Both water containing a significant amount of carbon dioxide and polluted water, however, can be more corrosive to aluminum.

6.2.3.2   Acid and Alkaline environments

Aluminum is resistant to neutral and acidic environments, in general, because of its ability to form an oxide film. However, aluminum is more prone to corrosion in alkaline environments. More specifically, aluminum has a general resistance to corrosion in environments with a pH in the range of 3 to 8.5. Under basic (alkaline) conditions the metal is attacked much more readily than the film. Thus, if the basic medium finds a hole in the oxide film, corrosion will occur usually in the form of pitting. Conversely, under acidic conditions the oxide film is attacked more readily than aluminum, thus, if corrosion occurs it will most likely be in the form of uniform corrosion. Corrosion inhibitors can expand the pH operating range of aluminum metals and alloys in alkaline environments up to approximately 11.5.

6.2.3.3   Soil

The corrosion resistance of aluminum and aluminum alloys in soil is dependent on the nature and conditions of the underground environment. In dry, sandy soil, aluminum and its alloys are sufficiently resistant to corrosion, but in wet, acidic or alkaline soils the metals are more susceptible to corrosion.

6.3   Copper and Its Alloys

Copper is a noble metal that has an inherent resistance to corrosion in a variety of environments. Despite its excellent corrosion resistance to a broad range of environments, copper corrodes rapidly in certain environments, unlike some other noble metals. Even so, it's good corrosion resistance generally applies to atmospheric environments, industrial environments, freshwater environments, and seawater environments, as well as a number of acidic and alkaline conditions. Pure copper is especially resistant to the aforementioned environments.

Copper is a low-cost alternative to stainless steels and nickel-base alloys when selecting a material for a corrosion resistant application. Copper alloys provide good strength at lower temperatures with a good resistance to corrosion in a broad range of environments. Among other applications, copper is useful for architectural applications (e.g. roofing), freshwater handling systems and plumbing, seawater handling systems, chemical process equipment and heat exchangers, and electrical systems.

6.3.1   <u>Alloys and Alloying Elements</u>

There are three main types of copper alloys: copper-tin (bronze), copper-zinc (brass), and copper-nickel (cupro-nickels). Each of these main alloys may be alloyed with additional elements, which in some cases provides increased corrosion resistance and improved material properties. The following sections briefly describe the corrosion characteristics of some common copper alloys.

6.3.1.1   Pure Copper and High-Copper alloys

Pure copper is accepted as having greater than 99% copper, while high-copper alloys have greater than 96% copper. Both pure copper and high-copper alloys have excellent resistance to corrosion, especially in seawater. They are also highly resistant to microbiological-influenced corrosion, as copper is toxic to microorganisms. They are, however, susceptible to erosion-corrosion.

6.3.1.2   Bronze

Alloying tin (Sn) with copper improves the resistance to corrosion in fresh water and seawater environments. Hence, bronze has an excellent corrosion resistance in fresh water and in contaminated water, as well as a very good resistance to corrosion in marine environments. Furthermore, alloys that contain approximately 8 to 10% tin have a good resistance to attack by impingement, which is a form of erosion corrosion. Bronze has moderate resistance to pitting corrosion. Moreover, the addition of tin to copper pushes copper more toward the cathodic end of the galvanic series, further protecting it from galvanic corrosion.

Aluminum is added in 5-12% to Cu-Ni-Fe-Si-Sn systems to make aluminum bronze alloys, which show improvements in general corrosion resistance and exhibit excellent resistance to impingement attack (erosion corrosion) and high temperature corrosion. With an aluminum content of less than 8%, aluminum bronze alloys have an excellent resistance to pitting. Aluminum bronze alloys can be used in nonoxidizing mineral acids, organic acids, neutral saline solutions, alkalis, seawater, brackish water and fresh water without being significantly

susceptible to corrosion.[73] They are not generally suitable, however, for use in nitric acid, metallic salts, humidified chlorinated hydrocarbons and ammonia.[73]

Phosphorous is added to copper-tin alloys to provide enhanced resistance to nonoxidizing acids (except HCl) and flowing seawater. These phosphor bronze alloys also have superior resistance to SCC compared to brass. The addition of silicon can make bronze susceptible to pitting, as well as embrittlement in the presence of high-pressure steam environments.[73]

6.3.1.3   Brass

Brass is a copper alloy with a significant zinc content. The content of zinc can be as great as about 40%, but corrosion by selective leaching (dezincification) can be significant when the content is more than 15%. The effect of zinc content on the susceptibility of brass to pitting and dezincification is shown in Figure 59. Copper alloys that have more than 85% copper are resistant to dezincification, but may also be more susceptible to corrosive attack by impingement. Low concentrations of zinc in brass leads to a very good resistance to pitting. The addition of zinc to copper moves it further down the galvanic series toward the anodic end, and therefore, it is more susceptible to galvanic corrosion. High zinc content can also lead to a greater susceptibility to SCC. Brasses with 20-40% Zn, for example, are highly susceptible to SCC, while brass alloys with less than 15% Zn are highly resistant to SCC. For marine environments, brasses with a copper content between 65 and 85% are the most resistant to corrosion. Copper-zinc alloys have a good resistance to corrosion in fresh water environments. The one type of brass that is considered to have the best corrosion resistance in fresh water is red brass (85% Cu, 15% Zn).
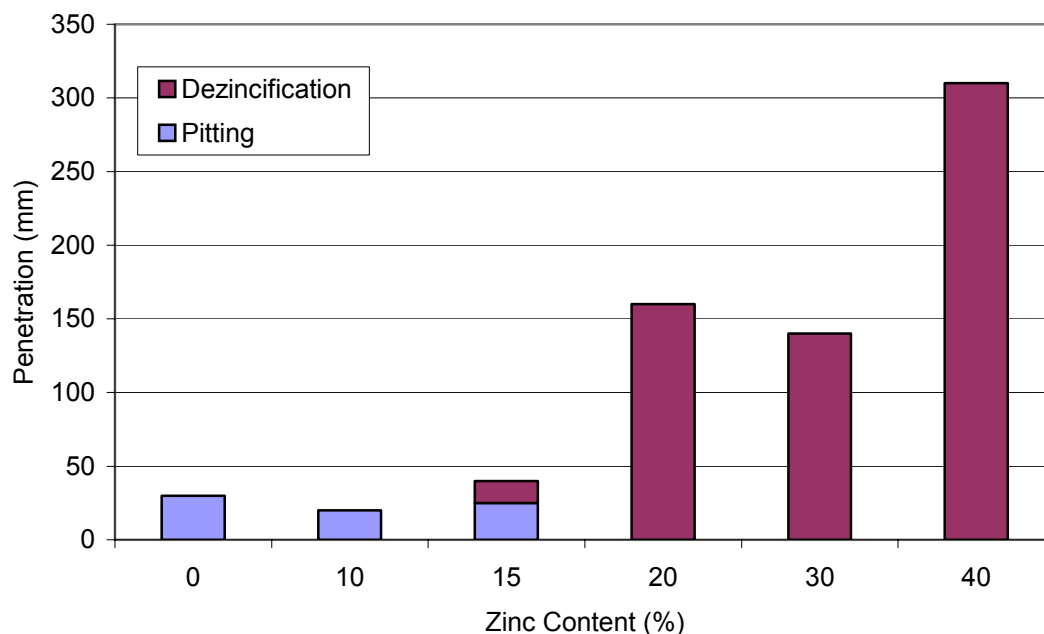
Figure 59   The Effect of Zinc Content on the Corrosion of Brass in an Ammonium Chloride Environment[73]

Alloying brass compounds with additional elements can enhance the corrosion resistance. The addition 1% Sn, for example, improves the resistance to dezincification in 70 Cu-30 Zn alloys; this alloy is called admiralty brass. (The addition of 0.75% Sn to 60 Cu-40Zn produces the alloy called Naval brass.) Alloying nickel with brass produces nickel-silver alloys, which have a good resistance to fresh water corrosion, are resistant to dezincification, and significantly improves corrosion resistance in salt water. The addition of Pb, Te, Be, Cr, or Mn to brass has no significant affect on its corrosion resistance.[73]

Al addition (2%) added to 76 Cu-22 Zn produces aluminum brass, which has improved corrosion resistance. These alloys exhibit improved resistance to impingement attack in seawater flowing at high velocities, but are still susceptible to dezincification.[73] The addition of arsenic, phosphorous or antimony can be used to increase the resistance of aluminum brass, admiralty brass or naval brass to dezincification.[73] Arsenic added to aluminum brass in an amount of approximately 0.10%, for example, improves dezincification resistance.

6.3.1.4   Copper-Nickel

Copper-nickel has a resistance to fresh water, contaminated water, and marine environments that is similar to that of bronze. It is also more noble than pure copper on the galvanic series, and therefore, less susceptible to galvanic corrosion. Copper-nickel alloys with a composition of 70% Cu and 30% Ni have the best resistance to corrosion in aqueous and acidic environments, in addition to having a very good resistance to SCC and impingement attacks. Copper-nickel alloys have a moderate resistance to pitting. Cu with 10% Ni also has a very good resistance to impingement attack and SCC. Copper-nickel alloys have a moderate resistance to pitting, although some specific alloys have an excellent resistance to pitting in seawater (e.g. alloys C70600 and C71500).[73] Copper-nickel alloys with additions of Fe are usually very resistant to SCC. Cu-18Ni-17Zn and Cu-18Ni-27Zn exhibit good corrosion resistance in freshwater and seawater, and a good resistance to dezincification.[73] Some copper-nickel alloys, however, are susceptible to crevice corrosion in seawater.

6.3.1.5   Other Alloying Elements

Copper-silicon alloys have a greater resistance to SCC than brass, in general. Copper-beryllium alloys are the only copper alloys that have shown a susceptibility to pitting in atmospheric environments. Additions of phosphorous in amounts greater than 0.04% can lead to serious SCC. Additions of aluminum result in a more anodic metal compared to pure copper, in terms of galvanic corrosion.

6.3.2   Resistance to Forms of Corrosive Attack

Despite its excellent corrosion resistance in general, copper and its alloys are susceptible to several forms of corrosion. Copper is susceptible, to some extent, to uniform corrosion, galvanic corrosion, dealloying (selective leaching), pitting, SCC, erosion corrosion, fretting, intergranular corrosion, and corrosion fatigue. These forms of corrosion with respect to copper and its alloys are described in the following sections. (They are also described in more general terms in Section 1.0.)

6.3.2.1   Uniform Corrosion

Copper and its alloys have a strong resistance to uniform corrosion under normal conditions, but over long periods of exposure they will exhibit to some extent this form of non-localized corrosion. Immersion in or uniform exposure to aerated or oxidizing acids or sulfur containing compounds, etc., will accelerate the process of uniform corrosion on copper and its alloys.

6.3.2.2   Galvanic Corrosion

Copper has a relatively noble (cathodic) position on the Galvanic Series compared to many structural metals and alloys, thus it will most likely not corrode preferentially when electrically coupled with one of them. When coupled with more noble metals, however, such as nickel, titanium, and some stainless steels, copper will corrode preferentially by galvanic action.

6.3.2.3   Dealloying (Dezincification)

When considering a copper alloy it is very important to realize its potential for dezincification, if it has a significant zinc content (>15% in Cu-Zn alloys). Dezincification is a process which leaches out the zinc leaving behind a less ductile, porous copper structure that is more susceptible to fracture. This often occurs in ambient waters or salt solutions. Dealloying also occurs in some copper-aluminum alloys, where the aluminum is selectively leached from the alloy. This has a greater occurrence in alloys with more than 8% aluminum.

6.3.2.4   Pitting

Most often, pitting does not occur to a significant extent in copper, that is, not enough to cause any considerable damage. If very thin copper or copper alloys are used, however, perforation is possible by pitting. Moreover, if copper is used in low flow velocity or stagnant seawater, it does have a slightly higher propensity for pitting.

6.3.2.5   Crevice Corrosion

Copper and its alloys are generally resistant to crevice corrosion, although a few specific alloys may have a tendency to experience a form of crevice corrosion. Typically, copper alloys containing aluminum or chromium have a higher susceptibility to crevice corrosion.

6.3.2.6   Erosion Corrosion

Copper and its alloys are susceptible to erosion corrosion, which is also characterized as impingement attack. This is especially the case for copper when immersed in polluted water, contaminated water, seawater, or water containing sulfur compounds. Erosion corrosion from cavitation also has a tendency to occur on copper alloys.

6.3.2.7   SCC

Copper and its alloys are susceptible to stress corrosion cracking, especially in the presence of ammonia and ammonium compounds. Stress corrosion cracking of copper alloys is presumed to be integrally related to dealloying.[73] Table 66 presents some copper alloys and their corresponding resistance to SCC.

Table 66   Resistance of Some Copper Alloys towards Stress-Corrosion Cracking[9]

Relative Rating	Alloy System
1. Low Resistance	• Brasses with more than 20% Zn • Brasses with more than 20% Zn plus small amounts of Sn, Pb, or Al (e.g., leaded high brass; naval brass; admiralty brass; aluminum brass)
2. Intermediate Resistance	• Brasses with less than 20% Zn (e.g., red brass; commercial bronze; gilding metal) • Aluminum bronze • Nickel (12%)-Silver
3. High Resistance	• Silicon Bronze • Phosphor-copper • Phosphor-bronze • Nickel (18%)-Silver
4. Superior Resistance	• Cupro-Nickel Alloys • Tough-pitch Copper • High-purity Copper

6.3.3 Corrosion Resistance in Various Environments

6.3.3.1 Atmospheric Environments

With the exception of instances where ammonia (NH_3), sulfur compounds (H_2SO_4) or certain other chemical agents are present, copper and its alloys generally exhibit an excellent resistance to corrosion in atmospheric environments, including clean (rural), polluted (industrial), marine and tropical. Copper and its alloys are therefore suitable for long-term use in atmospheric environments. Table 67 provides the corrosion rates of certain copper alloys in various atmospheric environments.

Table 67   Uniform Corrosion Rates of Some Copper Alloys in Several Atmospheric Environments[73]

Copper Alloy	Corrosion Rate (μm/year)					
	Industrial	Industrial Marine	Tropical Rural Marine	Humid Marine	Rural	Dry Rural
ETP Pure Copper	1.40	1.38	0.56	1.27	0.43	0.13
DLP Pure Copper	1.32	1.22	0.51	1.42	0.36	0.08
Red Brass	1.88	1.88	0.56	0.33	0.46	0.10
Cartridge Brass	3.05	2.41	0.20	0.15	0.46	0.10
Phosphor Bronze	2.24	2.54	0.71	2.31	0.33	0.13
Aluminum Bronze	1.63	1.60	0.10	0.15	0.25	0.51
Silicon Bronze	1.65	1.73	-	1.38	0.51	0.15
Tin Brass	2.13	2.51	-	0.33	0.53	0.10
Copper Nickel	2.64	2.13	0.28	0.36	0.48	0.10

ETP – Electrolytic Tough Pitch   DLP – Deoxidized Low Phosphorous

6.3.3.2   Water Environments

In fresh water environments, copper tends to form a protective coating on the surface, and is typically very resistant to corrosion in such environments. The corrosion rate is slightly higher in soft water or water having a significant amount of dissolved CO_2. Marine environments typically pose little threat to copper and most copper alloys, although at high flow velocities in seawater copper is very susceptible to erosion corrosion. Copper and its alloys are also very resistant to biofouling.

Copper is generally resistant to corrosion in steam environments. If there is a significant concentration of CO_2, oxygen or ammonia in the steam, however, the copper is more susceptible to corrosion.

6.3.3.3   Acids/Alkalines

Copper does not usually corrode in the presence of acids unless there are oxidizing agents (e.g. oxygen, HNO_3) available. For instance, copper and sulfuric acid do not react unless oxygen is present. Hence, it is susceptible to oxidizing acids, in addition to oxidizing heavy metal salts, sulfur, and ammonia. Exposure to environments containing ammonia can result in rapid and severe attack in the form of uniform corrosion or SCC. However copper is resistant to neutral solutions and solutions with a pH slightly on the alkaline side. The most threatening environments are ammonia, cyanide solutions, oxidizing salts and acids, or salts and acids in oxidizing conditions. Table 68 provides the uniform corrosion rate of copper in three different acids.

Table 68   Corrosion Rate of Copper in Several Acids[73]

Acid	Corrosion Rate (mils/year)
32% HNO_3	9450
Concentrated HCl	30
17% H_2SO_4	4

6.3.3.4   Soil

Copper is generally very resistant to corrosion in soil, and copper-tin (bronze) alloys are especially resistant to corrosion in soil. The presence of organic compounds, ammonium compounds, sulfates, or cinder, however, adversely affects the corrosion resistance of copper. Figure 60 shows the rate of uniform corrosion for copper in four different types of soils over a long period of time.

6.4   Nickel and Its Alloys

Nickel and nickel alloys are commonly used for applications subject to severe corrosion problems, since they exhibit excellent corrosion resistant properties in addition to having other desirable material properties. They are more expensive, however, than copper alloys and stainless steels. Nickel is a relatively noble metal, and does not readily corrode without the presence of an oxidizing agent. Under certain conditions nickel will form a passive film that protects the metal from corrosion.
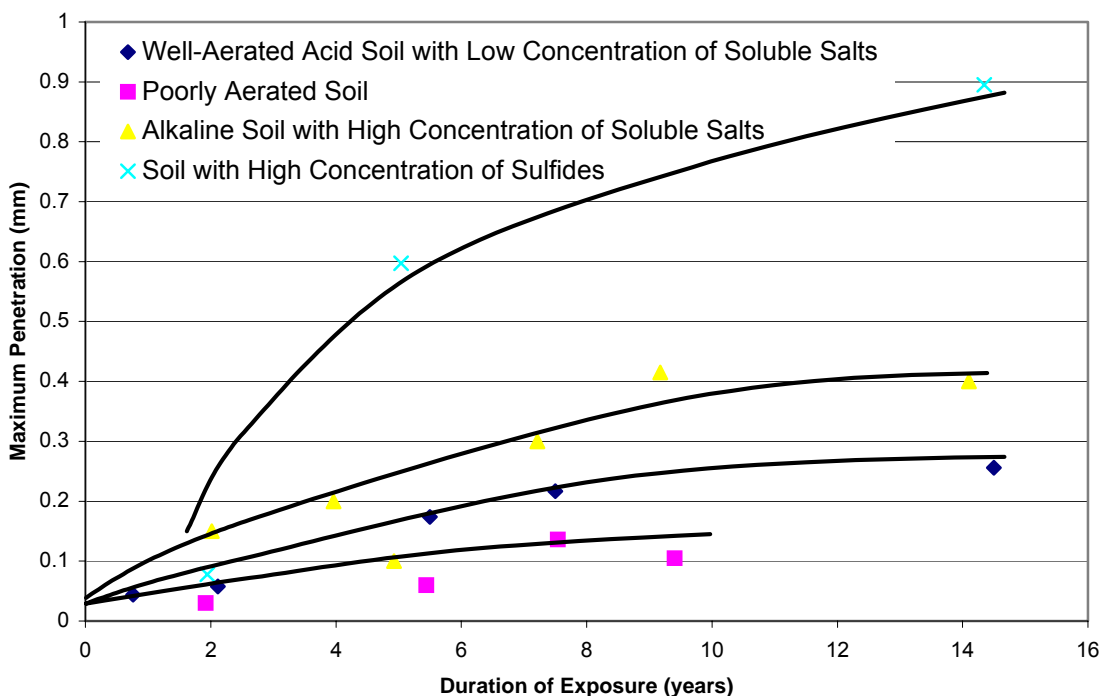
Figure 60   Rate of Corrosion of Copper in Different Types of Soils[73]

There is a wide range of environments that nickel and its alloys are resistant to. They typically show good resistance to corrosion in atmospheric environments, fresh water, distilled water, seawater and nonoxidizing acid environments. Nickel also has a very good resistance to corrosion in alkaline environments and solutions, halogens, reducing salts, and other oxidizing halides.[74] They have good resistance to corrosion at lower and higher temperatures, and in neutral solutions or solutions with a pH slightly less than 7. Nickel has a strong resistance to high stresses that may cause SCC. Nickel is susceptible to strong oxidizers (e.g. nitric acid, ammonia) and sulfuric environments at high temperature, however, which can cause general corrosion and possibly intergranular corrosion.

6.4.1   Alloys and Alloying Elements

Many of the superalloys are nickel-based or have a high nickel content, and have a good resistance to corrosion. Several of the key alloying elements and their impact on the corrosion resistance of nickel are reviewed in the following sections. In addition, some nickel-based alloys are considered as well.

6.4.1.1   Chromium

The addition of chromium enhances the resistance of nickel to high temperature corrosion. Chromium additions improve the resistance to oxidation at high temperatures and the resistance to oxidizing acids such as nitric and chromic acids. Furthermore, chromium improves the resistance of nickel to carburization and sulfidation at higher temperatures, but negatively impacts the resistance to corrosion in high temperature environments containing nitrogen or fluorine. Chromium forms a passive film on the nickel alloy in these types of environments. It

also provides resistance to corrosion in liquid environments at lower temperatures, and to SCC, pitting and crevice corrosion. The maximum corrosion resistance is achieved with a chromium content of approximately 20%, and corrosion resistant superalloys usually contain 15-30% Cr.

6.4.1.2   Nickel-Chromium-Iron Alloys

Inconel 600 is a Ni-Cr-Fe alloy that is very resistant to corrosion in organic acids, caustic soda, and alkalis, but is only moderately resistant to corrosion in mineral acids. It is also resistant to atmospheric corrosion, high temperature corrosion, SCC, oxidation, carburization and nitridation.[74] Hastelloy G-30 has excellent resistance to corrosion in nitric acid, and also resistant to sulfuric acid, phosphoric acid, fluorides, and oxidizing acids in general. Inconel 690 exhibits excellent resistance to oxidizing agents, sulfuric acid, and nitric acid. It is also very resistant to high temperature corrosion.

6.4.1.3   Nickel-Chromium-Molybdenum Alloys

Inconel 617 is a nickel-chromium-molybdenum alloy that exhibits excellent resistance to oxidation. Inconel 625 is resistant to pitting, crevice corrosion and oxidation at high temperatures, as well as to highly corrosive environments.[74] It also shows resistance to corrosion in halides, as well as to carburization, which can cause corrosive degradation of the material. Hastelloys C-276 and C-4 offer resistance to localized corrosion as well as SCC. Inconel 625 and Hastelloy C-276 can be resistant to hydrochloric acid even in the presence of oxidizing agents. Hastelloy C-22 provides superior resistance to oxidation, as well as excellent resistance to SCC and localized corrosion. Hastelloy C-2000 offers very good resistance to uniform corrosion in a wide range of environments, as well as very good resistance to SCC and localized corrosion.

6.4.1.4   Nickel-Chromium-Iron-Molybdenum Alloys

Incoloy 825 is a nickel-chromium-iron-molybdenum alloy that exhibits excellent resistance to sulfuric acid and phosphoric acid, moderate resistance to hydrochloric acid, and less resistance to corrosion in alkalis and halogens. Incoloy 825 is resistant to SCC, pitting and intergranular corrosion.[74] Hastelloy G and Hastelloy G-3 are suitable for service in sulfuric acid and phosphoric acid. Hastelloy G-30 is resistant to corrosion in phosphoric acid, sulfuric acid, nitric acid, fluorides, and oxidizing acids.[74] Hastelloy D-205 exhibits excellent corrosion resistance in sulfuric acid at high temperatures and to oxidizing agents. Most of the alloys in this group are very resistant to atmospheric corrosion.

6.4.1.5   Copper

Nickel-copper alloys have excellent resistance to corrosion in seawater, some acids, alkalis, and halides. Additions of copper typically improve nickel's resistance to nonaerated, nonoxidizing acids. For example, additions of 30-40% Cu typically result in nickel having a good resistance to sulfuric acid and an excellent resistance to hydrofluoric acid. Copper is the main alloying element in Monel superalloys, which contain approximately 70% Ni and 30% Cu and have a good resistance to hydrofluoric acid. Copper can be added to Ni-Cr-Mo-Fe alloys to improve their resistance to hydrochloric, sulfuric and phosphoric acids.[74]

6.4.1.6   Nickel-Copper Alloys

Nickel-copper alloys possess corrosion resistance similar to that of pure nickel, that is, they are resistant to corrosion in a broad range of environments. They are also similar to nickel in that they are susceptible to corrosion in oxidizing environments. Nickel-copper alloys have a good resistance to corrosion in sulfuric acid, seawater, and halogens.

Monel 400 is a nickel copper alloy with additional alloying elements, and is very resistant to seawater, sulfuric acid, alkalis, and halogen acids, including hydrofluoric acid as long as oxygen is not present in significant quantities.   The resistance of Monel 400 to corrosion in low concentrations of nonoxidizing hydrochloric acid is very good even at higher temperatures (up to 200°C). It is much more susceptible to corrosion in hydrochloric acid containing oxidizing agents. Monel 400 is also very resistant to atmospheric corrosion and to corrosion in flowing seawater. Monel 400 exhibits very good resistance to erosion corrosion in seawater, but is susceptible to pitting and crevice corrosion in stagnant or low-flow velocity seawater. Monel K-500 has corrosion characteristics similar to Monel 400.

6.4.1.7   Aluminum

Aluminum additions help to provide resistance to oxidation, sulfidation (which can cause corrosive degradation) and carburization at high temperatures, but may also make nickel more susceptible to high temperature corrosion in nitriding environments. With greater than 4% Al content, an oxidation inhibiting aluminum oxide film is capable of forming on the surface of the nickel alloy; however, it only occurs at high temperatures (>870°C). Once the film is formed it will protect against lower temperature oxidation too, but if it is abraded or removed, the alloy will no longer have the same oxidation resistance. Aluminum may result in a degradation of the hot corrosion resistance in superalloys, but it is also dependent on Cr content and the temperature of the environment.

6.4.1.8   Titanium

Additions of titanium to nickel are not typically used in nickel alloys intended for use in lower temperature applications. Titanium may provide some improvement in nickel's resistance to hot corrosion, but it may also degrade the resistance to SCC, if carbon, oxygen or nitrogen is present. Titanium additions are used in superalloys with aluminum to improve the strength, and a high titanium to aluminum content ratio results in improved hot corrosion resistance.

6.4.1.9   Molybdenum

Additions of molybdenum improve the resistance of nickel to crevice corrosion, pitting corrosion in seawater, and to corrosion in nonoxidizing acids. Up to 28% Mo is used for nonoxidizing environments of hydrochloric, phosphoric, hydrofluoric and sulfuric acids.   However, molybdenum also degrades nickel's resistance to hot corrosion and to nitric acid, and decreases the resistance of nickel to oxidation at high temperatures. Furthermore, nickel-molybdenum alloys are susceptible to corrosion in oxidizing acid environments.

6.4.1.10   Nickel-Molybdenum Alloys

Nickel-molybdenum alloys exhibit excellent corrosion resistance in hydrochloric, sulfuric, and phosphoric acid environments. They are however, more susceptible to corrosion in oxidizing environments, and are especially susceptible to corrosion in nitric acid environments.

Hastelloy B and Hastelloy B-2 exhibit good resistance to corrosion in hydrofluoric acid environments at low temperatures. Welded components made from Hastelloy B may be susceptible to intergranular corrosion. Hastelloy B-2 is a nickel-molybdenum alloy that has excellent resistance to aluminum-chloride environments, while Hastelloy B-3 exhibits good resistance to SCC. Both of these alloys exhibit superior resistance to corrosion in hydrochloric acid compared to all of the nickel-based alloys, but they are more susceptible to this environment if oxidizing agents are present.

6.4.1.11   Tungsten

Tungsten additions improve the resistance of nickel to localized corrosion and corrosion in the presence of nonoxidizing acids. Tungsten can quickly increase the density of a nickel alloy, however, because of its relatively high atomic weight. When used with 13-16% Mo in amounts of 3-4%, tungsten provides extra local corrosion resistance. However, alloying tungsten with nickel superalloys can result in a poorer resistance to hot corrosion. Tungsten may negatively affect the resistance of nickel to oxidation at high temperatures.

6.4.1.12   Silicon

Nickel alloys containing silicon often have it in small amounts as a contaminant from a processing step during fabrication. Silicon additions however, are sometimes intentionally used (typically 9-11%) to provide hot corrosion resistance in concentrated sulfuric acid environments. Moreover, silicon additions improve the resistance of nickel to high temperature corrosion; specifically oxidation, nitridation, sulfidation and carburization.[74]

6.4.1.13   Iron

Additions of iron can be used to reduce the cost of nickel, since nickel is more expensive than iron, but it does not offer much in terms of corrosion resistance. Iron additions, though, can improve nickel's resistance to sulfuric acid, and may also improve the resistance to carburization at high temperatures.

6.4.1.14   Cobalt

Cobalt is not typically used in significant amounts since it has corrosion resistance characteristics very similar to nickel and is more expensive. It does however, provide improvement to high temperature carburization and sulfidation resistance in nickel alloys.[74]

6.4.1.15   Other Alloying Elements

Yttrium, lanthanum, and other elements may also improve the corrosion resistance of nickel and its alloys. Yttrium generally improves the resistance to high temperature oxidation, sulfidation and carburization. Tantalum and niobium can improve the corrosion resistance at higher

temperatures and the resistance of nickel alloys to intergranular corrosion. Niobium may increase the resistance of nickel to carburization at high temperatures, but may also decrease the resistance of nickel to nitridation at high temperatures. Carbon can improve the resistance of nickel to nitridation and carburization at high temperatures, but decreases the resistance to high temperature oxidation. Manganese typically reduces the resistance of nickel to high temperature oxidation and nitridation.

6.4.2   Resistance to Forms of Corrosive Attack

In general, nickel and its alloys have an excellent resistance to corrosion. In certain conditions, of course, they may be susceptible to some forms of attack. A few of the forms of corrosion are described below in terms of the resistance or susceptibility of nickel and its alloys.

6.4.2.1   Uniform Corrosion

Nickel and its alloys are very resistant to general corrosion in a wide range of environments. Since it is a relatively noble metal, alloys with a high nickel content typically exhibit a good resistance to uniform corrosion.

6.4.2.2   Galvanic Corrosion

Since nickel is a relatively noble metal and also a fairly cathodic in the Galvanic Series (see Table 19) compared to most other metals, it is not very susceptible to galvanic corrosion. It may however, exhibit a degree of corrosion due to galvanic action, if it is coupled with a more noble metal.

6.4.2.3   Pitting and Crevice Corrosion

Nickel is somewhat susceptible to pitting and crevice corrosion in seawater and other environments. Typically, surface impurities are the cause of pitting, since they can act as a nucleating point for corrosion. Crevice corrosion can occur, particularly in areas where there is stagnant seawater.

6.4.2.4   Intergranular Corrosion

Nickel has a good resistance to intergranular corrosion, although in certain nickel alloys with inappropriate heat treatments it may be susceptible to this particular form of corrosion. In general, a higher nickel content corresponds to a better resistance to intergranular corrosion. In environments containing sulfur, nickel alloys have an increased susceptibility to intergranular corrosion.

6.4.2.5   Stress Corrosion Cracking

Alloys that contain mostly nickel with a small amount of iron tend to be susceptible to SCC. Nickel alloys seem to have a greater resistance to SCC compared to stainless steels.

6.4.2.6   High Temperature Corrosion

Nickel and its alloys may be susceptible to oxidation, carburization, nitridation, sulfidation and halogenation at high temperatures.[74] Certain alloying elements however, can provide augmented resistance to high temperature corrosion in environments where these contaminants are present.

6.4.3   Corrosion Resistance in Various Environments

6.4.3.1   Atmospheric Environments

Nickel and nickel alloys demonstrate very good resistance to corrosion in atmospheric environments, although after extended periods of exposure many alloys will develop a thin, adherent film, especially in industrial environments. Even so, nickel and its alloys are generally suitable for use in atmospheric environments, due to their strong corrosion resistance. Table 69 gives corrosion data on some nickel-based alloys after exposure to the atmosphere.

Table 69   Atmospheric Corrosion of Nickel-Base Alloys[74]

Alloy	Average Weight Loss/Surface Area (mg/dm^2)	Average Corrosion Rate (mils/year)
Nickel 200	468.6	<0.1
Incoloy 800	27.9	<0.1
Inconel 600	19.7	<0.1
Monel 400	644.7	<0.1
Incoloy 825	8.7	<0.1

6.4.3.2   Water Environments

Fresh water environments do not pose much of a threat to nickel and nickel alloys, since they generally exhibit a good corrosion resistance in these environments. Therefore, they are suitable for applications that require the exposure to or handling of fresh water environments.

The resistance of nickel and nickel-based alloys to corrosion in seawater is dependent on factors such as the velocity of flow of seawater. Some alloys may exhibit good corrosion resistance to flowing seawater, for example, but are susceptible to corrosion in stagnant or low-flow seawater. Table 70 shows the corrosion resistance of several nickel-based alloys exposed to stagnant seawater.

Table 70   Corrosion Resistance of Several Nickel-Based Alloys Exposed to Stagnant Seawater.

Alloy	Maximum Pit Depth (mils)
Inconel 625	-
Incoloy 825	0.98
Monel K-500	34
Monel 400	42
AISI type 316 Stainless Steel	62

6.4.3.3   Acids/Alkalis

Nickel and nickel-based alloys are generally resistant to corrosion in nonaerated and nonoxidizing acids. Since sulfuric acid is not considered to be an oxidizing acid up to a concentration of about 50-60 wt.%, for example, most nickel alloys are generally resistant to corrosion in this environment.[74] The corrosion rate of these alloys, though, typically increases with increasing sulfuric acid concentration. Nickel and its alloys are generally resistant to corrosion in acrylic acid and fatty acids.[74]

The presence of oxidizing agents in acids or the aeration of acids can significantly increase the corrosion rate of the nickel alloy. For instance, nickel alloys are typically resistant to HCl in low concentrations, but the presence of Cu^{2+} or Fe^{3+}, for example, may increase the corrosion rate of these alloys considerably. Some alloys, however, offer a better resistance in acids with oxidizing agents present, than others. Alloys containing chromium are more resistant to these types of acids, such as nitric and chromic acids, while molybdenum additions tend to degrade the resistance of nickel to these acid environments. The uniform corrosion rates of some nickel-based alloys in several acid environments are given in Table 71.

Table 71   Corrosion Rate of Several Nickel-Based Alloys in Various Acid Environments[74]

Nickel-Based Alloy	Corrosion Rate (mils/yr)		
	5% HF Acid	99% Acetic Acid	40% Formic Acid
Inconel 600	9.0	-	10.0
Hastelloy C-276	10.0	0.3	2.9
Hastelloy C-22	13.5	-	-
Hastelloy B-2	15.0	1.2	0.35
Hastelloy C-4	15.0	0.02	3.0
Inconel 625	16.0	0.4	7.3
Nickel 200	18.0	4.5	10.4
Hastelloy G	-	1.2	5.1
Hastelloy G-2	-	0.2	-
Hastelloy G-3	20.0	0.6	2.0
Hastelloy G-30	30.0	-	-
Monel 400	-	0.6	2.1
Incoloy 825	-	-	7.9

Nickel is strongly resistant to corrosion in alkalis, but environmental contaminants can cause an increase in the corrosion rate. Nickel is not, however, resistant to ammonium hydroxide solutions.[74] The corrosion resistance of nickel alloys in alkalis tends to decrease with decreasing nickel content.

6.5   Titanium and Its Alloys

Titanium is an inherently reactive metal, but it performs very well against a wide range corrosive environments. It may be the best available metal for corrosion resistance, but it is also very expensive, thus it is not used for many applications. This inherent corrosion resistance can be primarily attributed to a continuous, self-healing, protective oxide film, which forms in the presence of oxygen or water vapor. The protective film helps resist corrosion in oxidizing

environments. In environments that do not contain an oxygen source, however, titanium is susceptible to corrosion.

6.5.1   Alloys and Alloying Elements

In general, additions of large amounts of an alloying element reduce the corrosion resistance of pure titanium. Small amounts of palladium, platinum, and rhodium, however, increase the resistance to corrosion, including corrosion in moderate concentrations of hydrochloric and sulfuric acids. Additions of approximately 30% molybdenum improve the resistance to hydrochloric acid.

Other typical alloying elements used in titanium alloys include aluminum, chromium, iron, manganese, molybdenum, tin, vanadium, and zirconium. Aluminum additions above 6% causes a significant degradation in the SCC resistance, while titanium aluminide intermetallics may have increased resistance to oxidation and oxygen embrittlement. Additions of approximately 2% nickel improves crevice corrosion resistance in hot brine environments, but reduces the resistance to hydrogen embrittlement and also degrades the formability of titanium. Table 72 shows the resistance or various titanium alloys to SCC in a hot-salt environment.

Table 72   Relative Resistance of Titanium Alloys to Hot-Salt Stress Corrosion[3]

Least Resistance	Moderate Resistance	Most Resistance
Ti-5Al-2.5Sn (M.A.)	Ti-8Mo-8V-2Fe-3Al	Ti-4Al-3Mo-1V
Ti-12Zr-7Al	Ti-5Al-5Sn-5Sr-1Mo-1V	Ti-10Sn-5Zr-2Al-1Mo-0.2Si
Ti-8Al-1Mo-1V (M.A.)	Ti-6Al-2Sn-4Zr-2Mo	Ti-11.5Mo-6Zr-4.5Sn
Ti-5Al-5Sn-5Zr	Ti-5Al-2.75Cr-1.25Fe	Ti-8Mn
Ti-6Al-6V-2Sn	Ti-13V-11Cr-3Al	
Ti-5Al-1Fe-1Cr-1Mo	Ti-8Al-1Mo-1V (T.A.)	
	Ti-2Fe-2Cr-2Mo	
	Ti-4Al-4Mo	
	Ti-6Al-4V	

M.A. – Mill Annealed
T.A. – Triple Annealed

6.5.2   Resistance to Forms of Corrosive Attack

Titanium and its alloys typically exhibit an excellent resistance to corrosion. Titanium is generally resistant to oxidation, galvanic corrosion, SCC, corrosion fatigue, and erosion corrosion. A few of the forms of corrosion and their correlation to titanium are briefly discussed in the following sections.

6.5.2.1   Stress Corrosion Cracking

Titanium is susceptible to SCC in the presence of hot-salts or gaseous chloride ions and residual stresses. Severe SCC usually only occurs in the presence of hydrobromic acid or red fuming nitric acid at elevated temperatures; otherwise SCC is not much of a threat to titanium, which is also generally resistant to SCC in seawater, fresh waters and body fluids. Titanium has exhibited susceptibility to SCC in liquid and gaseous oxygen at cryogenic temperatures.

6.5.2.2   Pitting

The occurrence of pitting on titanium is rare, although it can result from iron adsorbed on the surface of titanium. Titanium resists pitting better than stainless steels and copper-nickels.

6.5.2.3   Other Forms

Titanium is susceptible to crevice corrosion, to liquid metal embrittlement in the presence of Cd and Ag, and is also susceptible to embrittlement as a result of the dissolution of hydrogen, oxygen, and nitrogen. Furthermore, titanium and its alloys have a high susceptibility to fretting at interfaces with titanium or other metals, which can significantly reduce its fatigue life.[43] Titanium does, however, have a strong resistance to erosion corrosion and impingement attack, as well as a good resistance to corrosion fatigue.

6.5.3   Corrosion Resistance in Various Environments

Titanium has an excellent resistance to atmospheric corrosion in unpolluted, marine, and industrial environments. It is also highly resistant to corrosion in water, seawater, and chloride solutions. In a wide variety of other chemical environments its corrosion resistance is similar to or better than most other metals. Furthermore, outstanding corrosion resistance at lower temperatures is characteristic of titanium.

Corrosion in inorganic salts and acids and ammonia solutions is easily resisted by titanium. The corrosion resistance of titanium in seawater and body fluids is superior to all other structural metals, and is therefore often used in orthopedic implants. Titanium is also resistant to hypochlorites, chlorine solutions, molten sulfur, wet chlorine gas, H_2S gas up to 260°C, and carbon dioxide up to 260°C. It is susceptible to dry chlorine gas and ionizable fluoride compounds (e.g. sodium fluoride, hydrogen fluoride). Furthermore, molten sodium hydroxide and hot, strong alkali solutions are a couple of the few substances which can attack titanium severely.

Titanium is resistant to most oxidizing acids and organic acids, but is susceptible to reducing acids, strong sulfuric and hydrochloric acids, phosphoric acids, oxalic acids, and fuming nitric acids. The corrosive effects of fuming nitric acid and chlorine gas, however, can be mitigated by adding small amounts of water. Moreover, oxidizing inhibitors and heavy metal ions are effective in mitigating the corrosive attack of acids.

6.6   Magnesium and Its Alloys

Magnesium has the lowest density of the metals but it also has the highest susceptibility to corrosion effectively eliminating it from use in most applications. An oxide layer will form on magnesium; however the thin film layers that form are usually soluble in water and readily breakdown in the presence of ions such as chloride and bromide. Increasing temperatures will also accelerate degradation of the protective film leading to widespread corrosion of magnesium. Galvanic corrosion of magnesium is always a consideration since it is anodic to most metals. Coatings should always be used to protect magnesium alloys in structural applications. Use of Mg alloys in moving components has led to rapid breakdown of the coating system leading to corrosion of the unprotected Mg alloy material. Therefore, magnesium alloys are almost entirely used in non-moving structural applications with proper protective methods.

6.6.1   Alloying for Corrosion Resistance

Alloying magnesium does not lead to any improvements in its corrosion resistance and in some cases can lead to a severe degradation in corrosion resistance. The effects of various alloying elements on the uniform corrosion rates of magnesium are shown in Figure 61.
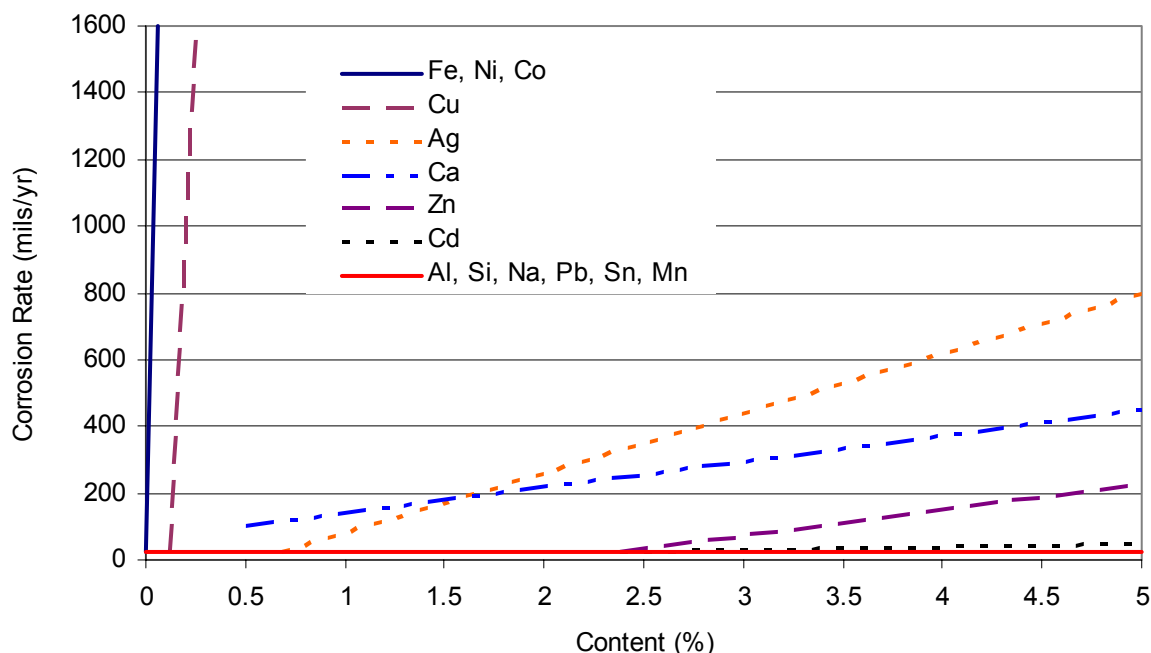
Figure 61   Effect of Alloying on the Uniform Corrosion Rate of Magnesium[75]

Iron, with a concentration of $\geq 0.017\%$, and also Ni, Co, and Cu significantly increase the corrosion rate of Mg. Aluminum improves the strength and hardness of Mg without seriously degrading its corrosion resistance. A content of 6% Al provides the best combination of strength and ductility. Although it may lead to an increase in corrosion rate, zinc is second to aluminum in its strengthening effect on Mg. It is used in combination with small amounts of other elements such as zirconium and the rare earths to produce a precipitation hardenable alloy. Zn also counters the corrosion effects of Fe and Ni contaminants found in Mg alloys. Manganese has been found to slightly increase resistance to salt water environments by interacting with iron and other heavy metal elements in the alloy. Mn has a low solubility in Mg and thus is used in small amounts, about 1.5% maximum and 0.3% with Al. Some common magnesium alloys with their respective applications are listed in Table 73.

Table 73   Common Magnesium Alloys[76]

Alloy	Alloying Elements	Applications	Remarks
AZ31	3.0 wt% Al 1.0 wt% Zn 0.2 wt% Mn	General purpose wrought alloy	Good extrudability
AZ91	9.0 wt% Al 0.7 wt% Mn	General purpose cast alloy	Good warm temperature mechanical properties
AZ81	8.0 wt% Al 0.7 wt% Mn	Automotive cast alloy	Air-cooled engines (high creep strength)
AM50	5.0 wt% Al 0.3 wt% Mn	High pressure die cast alloy	Automotive structural alloy
ZE41	4.2 wt% Zn 1.0 wt% RE* 0.7 wt% Zr	Special cast alloy for helicopter gearbox	Good creep strength at elevated temperatures
AS41	4.2 wt% Al 1.0 wt% Si 0.3 wt% Mn	Used for automotive crankcases	Better creep resistance than AZ91 at warm temperatures
QE22	2.5 wt% Ag 2.2 wt% RE* 0.7 wt% Zr	Sand and permanent mold casting alloy	Used in aircraft and missile housings
EZ33	3.0 wt% RE* 3.0 wt% Zn	Aluminum-free sand and permanent mold casting alloy	Excellent castability and pressure tightness; easily weldable
WE43	4.3 wt% Y 2.4 wt% RE*	Cast alloy for helicopter gearbox	Better creep resistance than AS41 at warm temperatures.

* rare earth element

6.6.2   Resistance to Forms of Corrosion

Magnesium and magnesium alloys can be highly susceptible to a number of corrosion forms including general corrosion. Issues unique to Mg alloys will be covered in this section. Corrosion prevention and protection methods are almost always necessary when using magnesium materials.

6.6.2.1   Uniform Corrosion

Magnesium alloys have the highest uniform corrosion rates of any metal as shown previously in

Figure 22 in Section 4.1-Uniform Corrosion. An oxide protective layer will form on magnesium once exposed, however this film is easily degraded by a number of environmental conditions and chemical compounds. Corrosion protection methods are almost always used with magnesium alloys. Magnesium alloys are not normally used in moving components where the coatings are easily damaged.

6.6.2.2   Galvanic Corrosion

All metals are cathodic to (more noble than) magnesium. Aluminum alloys are closest to magnesium in the galvanic series, although some aluminum alloys may still pose galvanic corrosion problems when in contact with magnesium alloys. Copper, nickel, and iron cause severe galvanic corrosion to magnesium, and thus aluminum alloys absent of these elements (5000 and 6000 Al series) are preferred for use when in contact with magnesium alloys. Aluminum alloys 5052, 5056, and 6061 have been found to have the least galvanic effect on Mg alloys in a marine atmospheric environment.[75]

6.6.2.3   Stress Corrosion Cracking

The SCC susceptibility of magnesium is generally more severe in alloys containing Al and/or Zn. The addition of aluminum, above 0.15 to 2.5%, creates the highest susceptibility in Mg alloys.[75] The susceptibility increases with increasing Al content to a peak at about 6%, see Figure 62. The addition of zinc increases SCC susceptibility, but not to the extent as does Al containing alloys. Mg alloys absent of both Al and Zn are the most resistant to SCC.
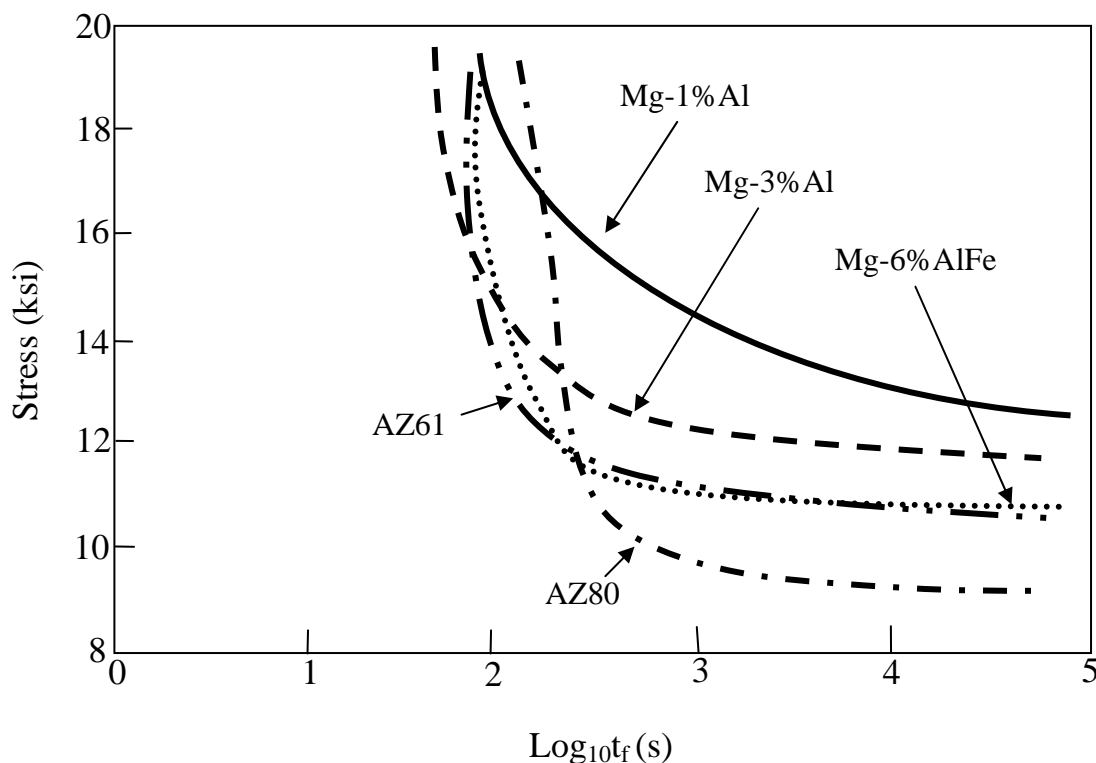
Figure 62   Stress versus Time to Failure for Mg-Al Alloys in a saltwater solution

6.6.3   Corrosion Resistance to Various Environments

Magnesium is susceptible to numerous environmental conditions. Only mild atmospheres and stagnant fresh water which do not break down the MgO surface layer on magnesium are acceptable for magnesium. Any agitation of the water environment or addition of salts into the environment will attack the protective coating and lead to corrosion of the magnesium. Humidity levels of 30% can produce mild corrosion with severe corrosion occurring at a level of

80%. All acids with the exception of hydrofluoric acid and H_2CrO_4 readily attack magnesium. Magnesium does resist corrosion in the presence of dilute alkalis. Organic acids, such as fruit juices and carbonated drinks severely attack magnesium. Other organic compounds do not affect magnesium at room temperatures but may lead to corrosion at elevated temperatures.

6.6.4 Corrosion Protection of Magnesium Alloys

Special care must be given to the fabrication of magnesium joints due to the high susceptibility of this metal. When joining two magnesium parts, a chemical conversion coating should be used, followed by one or more primer coats having alkali resistance such as an epoxy or vinyl resin. Fasteners for Mg-Mg joints include 5056 Al rivets, 6061 Al bolts, and cadmium or zinc plated steel bolts. For joining magnesium with a dissimilar metal, the surfaces must be insulated with an organic tape, sealing compound, or an alkali resistant paint. The joint should be fastened with cadmium plated steel bolts and nuts with a 5052 aluminum washer separating the steel and magnesium. Only 5056, 6061, and 6053 aluminum alloy bolts and screws can be used bare, to join magnesium. All other metal fasteners should be coated when used with magnesium. Some general procedures to limit corrosion in magnesium structures are listed in Table 74.

Table 74   Procedures to Limit Corrosion in Magnesium Structures

Procedure	Method
Eliminate areas where trapped moisture is held in contact with metal	Design them out in the first place by careful attention to design of structure details. Provide properly located drain holes. Minimum size about 3.2 mm to prevent plugging.
Choose nonabsorbent, nonwicking materials to contact magnesium	Determine water absorption qualities of materials to be used. Use epoxy and vinyl tapes and coatings, wax, or latex for protective barriers. Avoid use of wood, paper, cardboard, open cell foams, and sponge rubbers.
Protect all faying surfaces	Use proper sealing materials (tapes, films, sealing compounds) on all faying surfaces. Use primers. Lengthen continuous liquid path to reduce galvanic current.
Use compatible metals	For Mg-Al couples, 5000 and 6000 series Al alloys are most compatible For Mg-steel couples, plate steel with zinc, 80% Sn – 20% Zn, tin, or cadmium.
Select proper finishing systems	Choose chemical treatments, paints, plating on basis of service requirements. Service test system before setting up production run. Use past experience in similar applications as guide to choice.

6.7 Zinc and Its Alloys

Zinc is not commonly used without supplemental corrosion protection for corrosion resistant applications since zinc is located near magnesium on the Galvanic Series, and is thus very susceptible to corrosion. It is therefore very anodic to most metals, and will corrode preferentially when galvanically coupled with metals that are more cathodic. Often it is used as an anodic

coating to protect steel from corrosion. It is also used as sacrificial anodes for ship hulls, pipelines and other applications. Furthermore, zinc can act as a barrier coating that is resistant to mechanical and electrochemical degradation.

Impurities have a significant impact on the corrosion resistance of zinc, as they often cause the surface to be more susceptible to corrosion. Some impurities, however, such as aluminum, may result in slight improvements in the corrosion resistance of zinc by forming a protective film on the surface.

6.7.1   Alloying for Corrosion Resistance

Neither alloying additions nor impurities significantly affect the corrosion resistance of zinc under normal conditions. Additions of antimony in amounts of 0.03 to 0.07 % do tend to increase the corrosion rate of zinc in atmospheric environments, while copper in amounts less than 0.06% may increase the corrosion resistance of zinc. Variations in the content of lead, cadmium and iron, on the other hand, have little affect on the corrosion resistance of zinc.

6.7.2   Resistance to Forms of Corrosive Attack

Severe pitting is rarely a problem for zinc, since most instances of corrosion takes place uniformly along the surface of the metal. Stress corrosion cracking and corrosion fatigue also rarely occur in zinc, but it is somewhat susceptible to crevice corrosion.

6.7.3   Corrosion Resistance in Various Environments

Zinc has a good resistance to all types of atmospheres, but moist and acidic environments can be problematic for zinc in terms of corrosion. Weak and strong acids and strong bases tend to attack zinc more readily, but it is generally resistant to weak bases. Industrial environments can be corrosive to zinc, especially if the contain sulfur dioxides. Zinc is susceptible to corrosion by sulfur dioxide, chlorides, and low-grade glycerin, but it is resistant to dry chlorine and hydrogen sulfide.

The corrosion rate of zinc is dependent on temperature, pH, and oxygen concentration. There seems to be a strong relationship between corrosion and oxygen content, as it increases with increasing oxygen content in the environment. Zinc is corroded 8 times faster in water with oxygen gas present than in water with no gases. In oxygen deficient environments, pitting tends to occur, while oxygen abundant environments lead to more uniform corrosion. The corrosion rate of zinc is temperature dependent, and it increases rapidly from room temperature to about 60°C, then decreases significantly at 100°C.

Zinc is susceptible to environments containing organic vapors, which tend to attack the metal's surface. Organic substances therefore, may be very corrosive to zinc, if they produce organic vapors or other products such as sulfur or halogen compounds. Zinc does tend to be resistant, however, to anhydrous organic liquids with a neutral pH.

Zinc has a good resistance to water, but it is more susceptible to corrosion if oxygen or carbon dioxide is present, or if the water is at an elevated temperature, or if the water is strongly aerated or agitated. Furthermore, soft water attacks zinc more readily than hard water, and steam can also be damaging, if zinc is exposed to it in a continuous manner.

6.8   Cobalt and Its Alloys

Cobalt and cobalt-based alloys are very similar to nickel and nickel-based alloys in terms of corrosion resistance, but typically they are slightly more susceptible to corrosion compared to their nickel counterparts. Cobalt-based alloys have an inherent wear and corrosion resistance. Cobalt is not considered an oxidation resistant metal, especially since the oxidation rate is generally about 25 times that of nickel. Cobalt-based superalloys, however, are resistant to oxidation and hot corrosion. Furthermore, the cobalt superalloys are more resistant to hot corrosion than are the nickel superalloys. Nickel and cobalt superalloys have a similar resistance to aqueous corrosion at lower temperatures.

6.8.1   Alloys and Alloying Elements

6.8.1.1   Chromium

Chromium is typically alloyed with cobalt in significant amounts to improve various properties of the metal, including corrosion and oxidation resistance. Cobalt superalloys generally contain 20-30% chromium, which contributes to their good oxidation and hot corrosion resistance. It also provides resistance to corrosion at lower temperatures, as well as higher temperature resistance to oxidation and hot corrosion. Moreover, chromium additions provide enhanced protection of cobalt-based alloys against corrosion in dilute nitric acid environments, but may also decrease the resistance to corrosion in high concentrations of nitric acid. Cobalt-based alloys with a significant chromium content are susceptible to corrosion in chromic acid environments. Cobalt-chromium alloys with a high carbon content also have good wear resistance, but carbon can also inhibit the beneficial effects of the chromium additions.

6.8.1.2   Nickel

Nickel additions improve the resistance of cobalt to corrosion in mineral acids, such as sulfuric and phosphoric acids. It also improves the resistance to SCC. Furthermore, nickel additions provide improved resistance to corrosion in caustic environments.

6.8.1.3   Tungsten

Tungsten additions can improve the resistance of cobalt to corrosion in general, but may lead to corrosion problems at temperatures above 980°C. Tungsten may also increase the corrosion resistance of cobalt-based alloys in chromic acid.

6.8.1.4   Other Alloying Elements

Copper additions improve the resistance of cobalt to corrosion in sulfuric and phosphoric acid conditions. Molybdenum additions can improve the resistance of cobalt to corrosion in general. Additions of vanadium and niobium can be detrimental to the cobalt alloys in terms of corrosion resistance, while additions of manganese, iron, yttrium and lanthanum can improve the alloy.

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6.8.2 Resistance to Forms of Corrosive Attack

Cobalt is susceptible to pitting and crevice corrosion, and is usually very resistant to SCC in many environments, but at higher temperatures (>150 °C) in acid chlorides and strong bases it may experience stress corrosion cracking.[77] Cobalt based alloys have an excellent resistance to erosion corrosion, especially from cavitation, and they also typically have outstanding resistance to high temperature corrosion. The resistance of cobalt alloys to oxidation and carburization at high temperatures is generally very good, and the resistance to sulfidation is better than that of nickel-based alloys. Furthermore, cobalt-based alloys tend to be more resistant to hydrogen embrittlement compared to their nickel counterparts.

6.8.3 Corrosion Resistance to Acids and Alkalis

Cobalt-based alloys are generally resistant to corrosion in aqueous environments. Cobalt-based alloys are very susceptible to corrosion in phosphoric acid, but are resistant to corrosion in acetic acid environments. The corrosion resistance of cobalt-based alloys is improved in sulfuric acid environments when oxidizing agents are present. Cobalt-based alloys are typically more resistant to nitric acid, but more susceptible to corrosion in caustic environments than their nickel counterparts.

6.9   Refractory Metals

Refractory metals have very high melting points, retain their strength at high temperatures, and accordingly are often used for jet engine and space applications. Several of the refractory metals and their corresponding melting points are given in Table 75. Refractory metals are typically susceptible to oxidation at high temperatures, but resistant to corrosion in many environments at lower temperatures.

Table 75   Melting Points of Several Refractory Metals

Metal	Melting Point (°C)
Tungsten	3410
Tantalum	2996
Molybdenum	2610
Niobium	2468
Zirconium	1852

6.9.1 Molybdenum

At high temperatures (approximately 700°C) in air, molybdenum forms a volatile oxide (MoO_3). It does not perform well in the presence of oxidizing agents at temperatures greater than 500°C, and requires protective coatings in order to be used practically in such environments. Molybdenum does, however, have a good resistance to hydrofluoric, hydrochloric and sulfuric acids without the presence of oxidizing agents. It has a good resistance to corrosion in low to moderate concentrations of sulfuric acid at low to moderate temperatures. Molybdenum is susceptible to oxidizers (e.g. nitric acid), and are generally resistant to alkaline solutions, although not in the presence of oxygen or oxidizing agents.

6.9.2   Tantalum

Tantalum is a fairly inert and expensive metal that is durable and long lasting with a very good resistance to corrosion in many environments including severe ones. Its corrosion resistance can be at least partially attributed to the thin, protective oxide film (usually Ta_2O_5) that forms when exposed to air or another oxidizing environment at 300°C. Its corrosion resistance, in general, is better than that of niobium. It is, however, embrittled in oxygen at temperatures greater than 350°C.

Tantalum is resistant to fresh water, mine water, deionized water and seawater; it is also resistant to steam at high pressures. It is highly resistant to most acids (e.g. sulfuric (H_2SO_4), nitric (HNO_3), hydrochloric (HCl), hydrobromic (HBr), etc.), chemical solutions, salts and salt solutions, and organic compounds including alcohols, ketones, alkaloids and esters, and is fairly resistant to dilute alkaline solutions.

Tantalum reacts with gaseous oxygen, nitrogen, and hydrogen at higher temperatures. It is susceptible to corrosion in hydrofluoric acid, hot concentrated phosphoric acid, sulfite (SO_3), strong alkalis, and strong sulfuric acid at higher temperatures. Tantalum is also susceptible to hydrogen embrittlement, if it is not protected from becoming cathodic in an electrochemical cell that produces atomic hydrogen. The reason for this is because tantalum will absorb hydrogen when it is galvanically coupled with anodic metals.

6.9.3   Niobium

Niobium is a refractory metal that has characteristics very similar to tantalum, which is located below it on the Periodic Table. It oxidizes readily, especially in air above 200°C, and forms a protective oxide film that provides good corrosion resistance.

Embrittlement of niobium is a problem in hydrogen, nitrogen, oxygen, or carbon at temperatures greater than 300°C. Niobium reacts with nitrogen at temperatures greater than 350°C, water vapor at temperatures greater than 300°C, chlorine at temperatures greater than 200°C, and hydrogen, carbon monoxide and carbon dioxide at temperatures greater than 250°C.

In general, niobium has a good resistance to both mineral and organic acids, but is susceptible to alkaline solutions. Specifically, it is resistant to hydrochloric, hydroiodic, hydrobromic, nitric, sulfuric and phosphoric acids; it is susceptible, however, to corrosion in hydrofluoric acid, and strong sulfuric and hydrochloric acids at higher temperatures. It is also less resistant to hot mineral acids compared to tantalum.

Niobium exhibits a good resistance to most gases at temperatures up to 100°C. It is also resistant to liquid and vaporous metals and molten salts. Furthermore, neither salt solutions nor seawater readily attack niobium.

6.9.4   Tungsten

Tungsten is extraordinary because it has the highest melting point of any metal. Besides its high temperature capability, it is resistant to corrosion in weak acids and alkalis at lower temperatures, but it is somewhat susceptible to strong acids at lower temperatures. Moreover, tungsten is susceptible to corrosion by alkalis and strong acids at high temperatures, and the attack can be accelerated or possibly more severe in the presence of oxidizing agents. Tungsten is highly

resistant to atmospheric corrosion and to corrosion in water. Oxidation is insignificant in air below 595°C or in oxygen at temperatures less than 510°C.[9]

6.9.5   Zirconium

Zirconium is an expensive and fairly reactive metal that is similar to hafnium, which is below it on the Periodic Table. A self-healing oxide film forms readily on the surface of zirconium in environments with available oxygen; this film protects against corrosion and wear. Zirconium is generally resistant to water and water vapor at regular and higher temperatures, although prolonged exposure to hot water may lead to rapid corrosion of the metal. It is also resistant to salt solutions, seawater, and polluted water. More specifically, zirconium is resistant to uniform, pitting and crevice corrosion in seawater.

Zirconium is also resistant to many acids and bases, including most mineral and organic acids and strong alkalis. Specifically, it is resistant to hydrochloric, nitric, acetic, formic, citric, lactic, and tannic acids, among others. Zirconium is susceptible to hydrofluoric acid, chromic acid and strong hydrochloric and sulfuric acids at higher temperatures. Its resistance to alkalis remains, even at higher temperatures, and has only a moderate corrosion rate when exposed to fused alkalis and liquid sodium.

Ferric chloride ($FeCl_3$) and cupric chloride ($CuCl_2$) environments will often cause pitting to occur on the surface of zirconium, but it is resistant to some molten salts. In general, zirconium is resistant to oxidizers in the absence of halides, but it is susceptible to corrosion, for example, in a humidified chlorine gas. A further threat to zirconium is hydrogen embrittlement.

Impurities in the composition influence the corrosion resistance of zirconium. For example, impurities such as nitrogen, aluminum, titanium, and dissolved ferric and cupric chlorides) degrade the resistance of zirconium to water and steam. Nuclear grades of zirconium do not contain hafnium and have better corrosion resistance in water at higher temperatures.

6.10 Beryllium

Beryllium is used in the nuclear industry, jet and rocket propulsion systems, mirror and re-entry vehicle structures, and aircraft brakes. It is virtually unaffected in normal atmospheric conditions even at elevated temperatures. Condensation on Beryllium can pose a corrosive attack under certain circumstances.

6.10.1   Effect of Impurities

Beryllium is produced in several grades, although none include intentional alloy elements. The production of Beryllium is controlled to reduce impurities present. Commercial grade Beryllium typically contains between 1 and 4.5 % total impurity content. Impurities on the surface of Beryllium through fabrication, cleaning, and machining can increase rates of corrosion. Carbides (Be_2C), introduced through machining, as well as chlorides and sulfates, introduced during a drying process, have resulted in corrosive attack of Beryllium. Improper handling in the form of fingerprints left on dry Beryllium has also led to corrosion. It is essential to control the processing and handling of Beryllium to limit impurities in and on the surface of the finished product.

6.10.2 Resistance to Forms of Corrosive Attack

There is a limited amount of published literature on the corrosion of Beryllium with the following information found.

6.10.2.1   Pitting Corrosion

Pitting corrosion of Beryllium has been seen to occur in some components prompting an investigation of the source mechanisms. It was found that pitting occurred in areas rich in aluminum, silicon, and iron impurities on the material's surface.

6.10.3 Corrosion Resistance in Various Environments

The susceptibility of Beryllium is primarily a result of corrosive chemicals, namely chlorides, sulfates, and nitrites present under humid conditions. A controlled humidity environment for storage has been found to be effective in limiting corrosion of Beryllium components.

6.10.4 Corrosion Protection of Beryllium

Coatings used on beryllium for corrosion resistance include anodic coatings, chromate, fluoride, and organic paints.[78] Anodic coatings, similar to those used in anodizing aluminum alloys, have been found to increase corrosion resistance in aqueous solutions and for elevated atmospheric temperature environments. Chromate coatings provide protection during storage and handling periods and in marine type environments for moderate periods. Fluoride coatings are used in distilled water and saltwater environments. Organic paints are used to provide an electrical insulation layer. This limits galvanic attack and has been observed to provide long term storage protection when deposited on top of a passivation type coating. Plated coatings have also been used on beryllium, providing electrical contacts, improved wear resistance, and better polishing surfaces.

6.11 Uranium

Depleted uranium is primarily used in weapon systems for its high density. With some alloying, the corrosion resistance is increased in various environments. Two forms of corrosion of which uranium alloys have showed a higher susceptibility, are galvanic and stress corrosion cracking. Protective measures used for uranium alloys have been oxide coatings, organic films, and metal platings.

6.11.1 Alloys and Alloying Elements

The corrosion resistance of uranium is increased with the addition of some alloying elements. The most common alloying elements are titanium, molybdenum, niobium, and zirconium. The addition of these elements promotes the formation of γ-phase (cubic) rather than the α-phase (orthorhombic) of unalloyed uranium, which increases the corrosion resistance.

6.11.2 Resistance to Forms of Corrosive Attack

6.11.2.1   Galvanic Corrosion

A measure of the electrode potentials of a few uranium alloys was obtained in both seawater and 0.1 N HCL. These values are used to determine the potential for galvanic corrosion in similar environments, when in contact with dissimilar metals as covered in Section 4.2. Table 76 gives the values measured in the two environments.

Table 76   Electrode Potentials of Uranium Alloys in Seawater and HCl[79]

Alloy	0.1 N HCl Electrode Potential (mV)		
	Oxygen Saturated (25ºC)	Air-equilibrated	
		(25ºC)	(70ºC)
Unalloyed Uranium	-740	-755	-790
U-4.5Nb	-465	-475	-600
U-6Nb	-395	-420	-465
U-8Nb	-375	-400	-445
U-7.5Nb-2.5Zr	-305	-340	-410
U-10Mo	-170	-190	-240
Alloy	Seawater Electrode Potential (mV)		
	Oxygen Saturated (25ºC)	Air-equilibrated (25ºC)	
Turballoy (Depleted Uranium)	-770	-795	
U-4.5Nb	-525	-530	
U-6Nb	-470	-460	
U-8Nb	-430	-415	
U-7.5Nb-2.5Zr	-370	-	
U-10Mo	-300	-	

6.11.2.2   Stress Corrosion Cracking

Stress corrosion cracking has been found to be problematic with uranium alloys. The U-0.75Ti alloy has the highest susceptibility, with SCC also occurring for the U-Mo and U-Nb alloys. The study of U-0.75Ti alloy in varying environments showed water to be the primary variable responsible for SCC with oxygen deterring SCC. The U-Mo alloys revealed susceptibility for Mo concentrations of 0.6-12%.   From 0.6 to ~5%, metastable materials were produced containing the α-phase, showing greater susceptibility to SCC. Above 5%, oxygen is the primary variable responsible for SCC, just the opposite as for the U-0.75Ti alloy. Increasing carbon content in the U-Mo alloys also produces increased susceptibility.   Heat treating quenched alloys produced a more equilibrium microstructure, proving to be less susceptible. Uranium-niobium alloys showed water induced susceptibility for the lower content Nb alloys (2.3 and 4.5%) and oxygen induced susceptibility for the higher content alloys (6 and 8%). Water vapor further increases the rate of attack for the U-6Nb and U-9Nb materials in an oxygen environment. The U-7.5Nb-2.5Zr alloy has been observed to form intergranular cracking which is easily propagated in the presence of oxygen, water, and chloride. Transgranular cracking has

also been seen for U-7.5Nb-2.5Zr in oxygen environments, but propagates slowly. The standard aging temperature for this alloy is 150ºC, showing the slowest crack propagation rates.

6.11.3 Corrosion Resistance in Various Environments

The methods to study corrosion of uranium alloys have primarily been through the thermodynamics and kinetics of corrosion science as covered in Section 9.0. There has been some limited corrosion testing on uranium, such as in seawater environments.

6.11.3.1 Atmospheric Environments

Corrosion of uranium and uranium alloys will react in humid air environments by the reaction:

$$U + (2+x) H_2O \rightarrow UO_{2+x} + (2+x)H_2 \qquad \text{Equation 12}$$
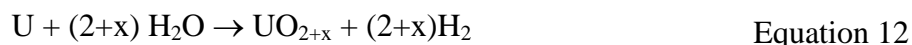
where $0 \leq x \leq 0.1$. The generation of hydrogen of various uranium alloys in a 100% relative humidity, 75ºC environment, is presented in

Figure 63.
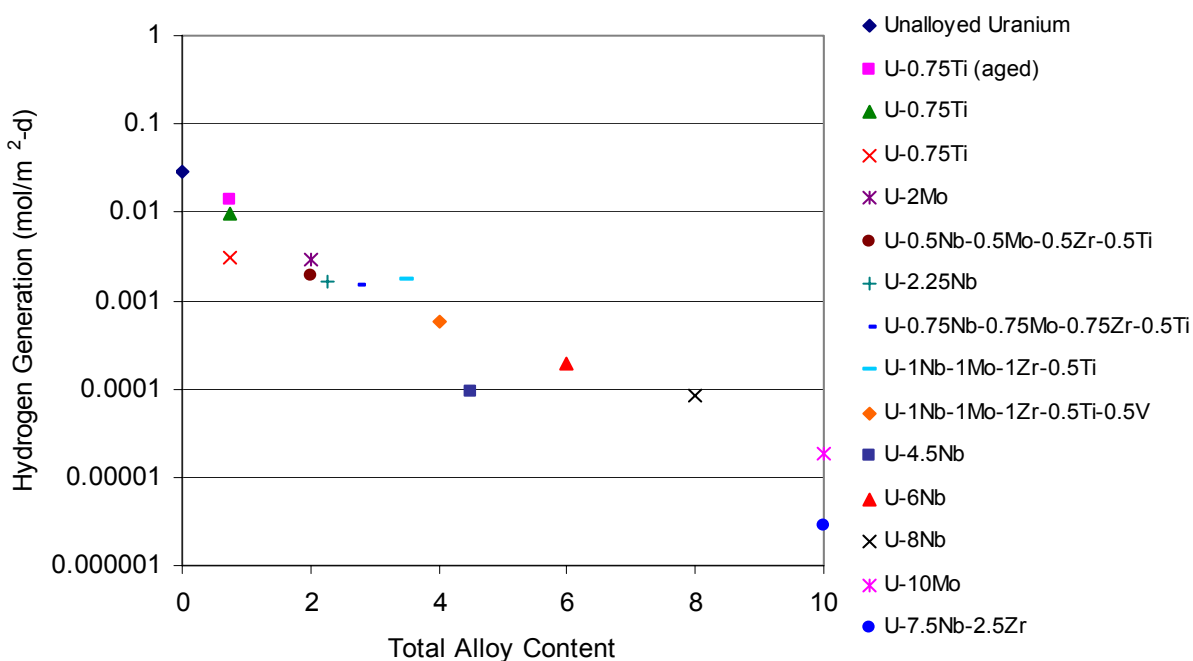
Figure 63   Hydrogen Generation of Various Uranium Alloys[79]

6.11.3.2 Water Environments

A similar dependence of alloying effect on the corrosion of uranium in water environments takes place. Measurements of the uniform corrosion rates of some uranium alloys and unalloyed uranium in seawater at 20ºC is shown in Figure 64.
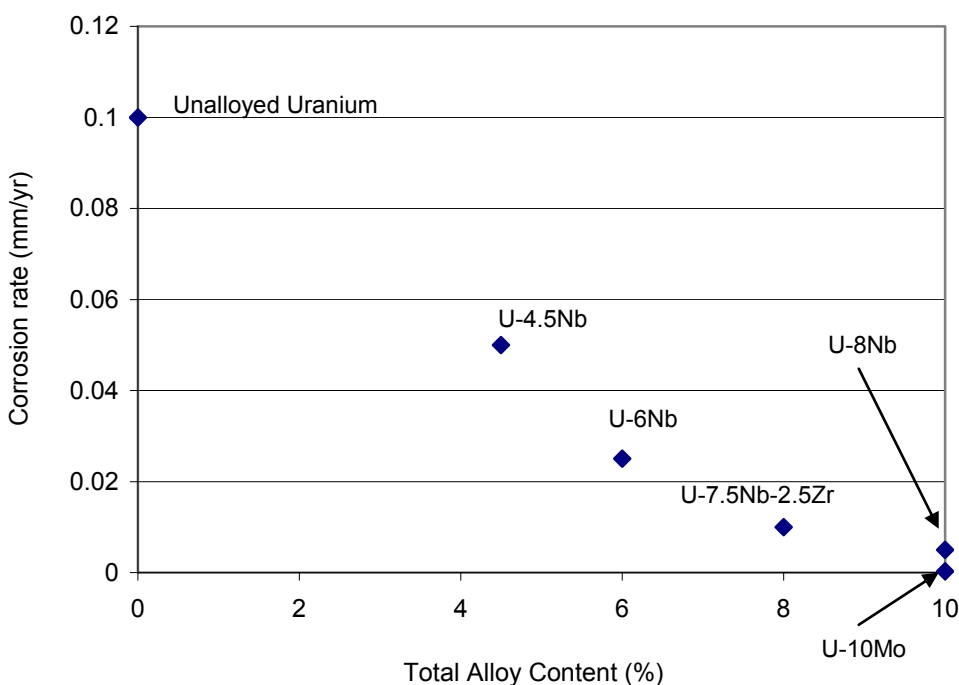
Figure 64   Uranium Alloy Uniform Corrosion Rates in Seawater[79]

6.11.3.3   Chemical Environments

The uranium-binary alloys show active-passive behavior in a number of chemical environments. The ion U^{3+} forms an active region, while UO_2^{2+} forms the passive region near the corrosion potential. Anodic polarization methods are used to study the active-passive transitions in uranium. The transition from active to passive generally represents a decrease in corrosion rate on the order of 10^4 to 10^6.

6.11.4 Corrosion Protection of Uranium

Materials and methods to provide corrosion protective coatings on uranium were studied primarily on unalloyed uranium. Ceramic oxides, organic films and metal platings have all been studied. The ceramic oxides and organic coatings tested have shown a minimal decrease up to increased uniform corrosion rates over unalloyed uranium. Metal platings, namely electroplated nickel and ion-plated aluminum have been found to decrease uniform corrosion rates in short-term slightly elevated temperature tests.

6.12 Cast Irons

Cast iron generally consists of alloying with >2% carbon and >1% silicon with various additional alloying elements dependent upon the application. Cast irons are among the lowest cost metals as they have low raw material costs and are more easily manufactured into product forms. They may be alloyed for corrosion resistance obtaining levels similar to that of stainless steels and nickel-based alloys.

6.12.1 Alloying for Corrosion Resistance

Cast irons can be classified by the degree of alloying into unalloyed gray, ductile, malleable, and white cast irons, low to moderately alloyed cast irons, and high-nickel, high-chromium, and high-silicon cast irons. The unalloyed irons consist of ≤3% of carbon, ≤3% silicon, with no additional intentional alloying. The corrosion resistance of this class is slightly higher than that of the unalloyed steels. The low to moderate alloyed irons include additions of chromium, nickel, copper, and/or molybdenum. They typically have two to three times the corrosion resistance of the unalloyed irons. The high alloyed cast irons have a high corrosion resistance to certain acid and alkali environments. High alloying for corrosion resistance may however compromise other material properties, such as a lower strength.

Alloying with silicon, nickel, chromium, copper, molybdenum, and to lesser extent, titanium and vanadium, will increase corrosion resistance. The alloying elements along with their associated effects on corrosion resistance are presented in Table 77.

Table 77   Cast Iron Alloying Elements and Their Effects[8]

Alloying Element	Effect
Silicon	▪ 3 – 14% results in some increased corrosion resistance ▪ > 14% results in a significant increase in corrosion resistance but with a decrease in strength and ductility ▪ >16% results in brittleness and manufacturing difficulties
Nickel	▪ Up to 4% in combination with chromium results in increased corrosion resistance and strength ▪ Corrosion resistance to both acids and alkalis increases ▪ ≥ 12% needed for optimal corrosion resistance ▪ ≥ 18% austenitic irons are practically immune to alkali and caustics, with increased SCC.
Chromium	▪ Small additions result in increased resistance to seawater and weak acids ▪ 15 – 30% increases resistance to oxidizing acids such as nitric acid ▪ High additions decrease ductility
Molybdenum	▪ Added to high silicon cast irons for increased resistance especially effective against hydrochloric acid ▪ 3 – 4% optimal concentration
Copper	▪ 0.25 – 1% increases resistance to dilute acetic, sulfuric, and hydrochloric acids, as well as acid mine water. ▪ ≤10% made to high nickel/chromium cast irons to further increase corrosion resistance.

6.12.2 Resistance to Forms of Corrosion

Cast irons will exhibit the same forms of corrosion as other metals. Notable susceptibilities found in the literature, specific to cast irons will be covered in the following sections.

6.12.2.1   Uniform Corrosion

The corrosion resistance of unalloyed cast irons slightly exceeds that of unalloyed cast steels, with increased resistance dependent upon the extent of higher alloying content, as discussed in Section 6.12.1. Figure 65 depicts the uniform corrosion rates of some cast irons in relation to a cast steel alloy.
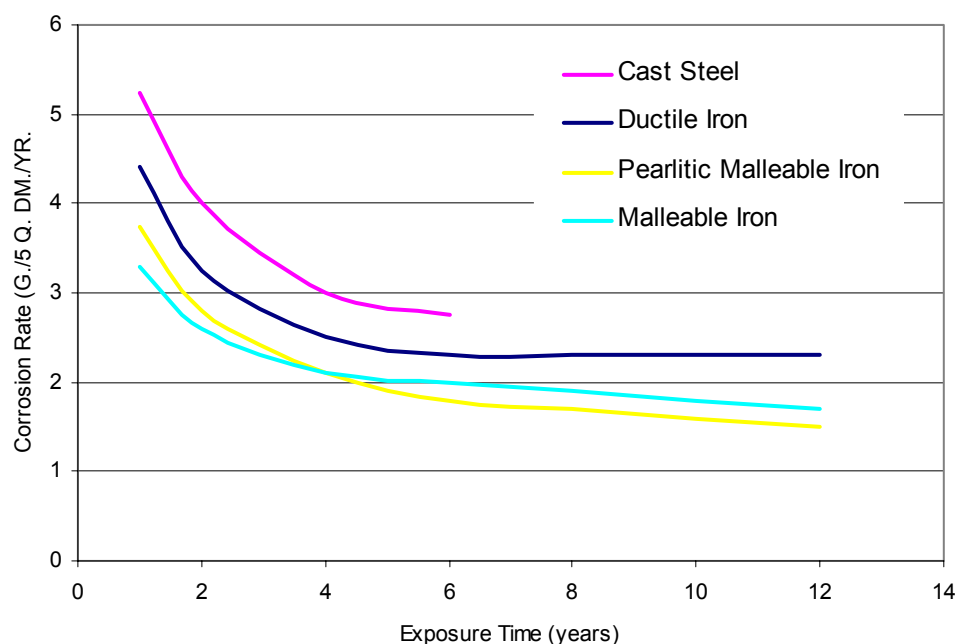
Figure 65   Uniform Corrosion Rates for Ferrous Metals Exposed for Twelve Years[80]

6.12.2.2   Galvanic Corrosion

Gray irons have microstructures conducive to galvanic attack in mild environments. The attack has been termed "graphitic corrosion" and has been classified as both galvanic corrosion and selective leaching. Graphite is cathodic to iron which leads to a localized galvanic cell within gray irons, which in turn leads to selective leaching of the iron. This form of attack only occurs in mild environments as more severe environments produce a more uniform corrosion where the graphite is also removed from the surface of the gray iron.

6.12.2.3   Fretting Corrosion

Fretting corrosion has been observed in a number of metals when in contact with cast irons. Table 78 summarizes field experience in fretting resistance of cast irons to other various materials.

Table 78   Fretting Resistance of Cast Irons to Various Materials[81]

Poor	Average	Good
Aluminum Magnesium Chrome plate Laminated plastic Bakelite Tin plate Shellac coated cast iron	Cast iron Copper Brass Zinc Silver plate Copper plate Amalgamated copper plate	Phosphate coated cast iron Rubber cement coated cast iron Tungsten sulfide coated cast iron Rubber gasket with cast iron Molykote lubricant with cast iron Molykote lubricant with stainless steel

6.12.2.4   Pitting Corrosion

Pitting of cast irons has been reported for environments that included chlorides, dilute alkylaryl sulfonates, antimony trichloride, and calm seawater. High silicon cast irons, especially those containing chromium and/or molybdenum have been found to exhibit a higher resistance to pitting. Nickel additions to cast irons increase pitting resistance for calm seawater environments.

6.12.2.5   Crevice Corrosion

The presence of chlorides in crevice areas of cast irons will increase the rate of crevice corrosion. High silicon cast irons with chromium and/or molybdenum provide higher resistances to crevice corrosion.

6.12.2.6   Intergranular Corrosion

Intergranular attack in cast irons is rare. The only instance found involves an attack of unalloyed cast iron by ammonium nitrate.

6.12.2.7   Erosion Corrosion

The resistance of cast irons to erosion corrosion may be enhanced by increasing the hardness and/or increasing some alloying elements. In relatively non corrosive environments, increasing the hardness through solid-solution or phase transformation induced hardening can increase erosion corrosion resistance. Higher alloying content combined with a higher hardness will increase resistance in more corrosive environments.

6.12.2.8   Stress Corrosion Cracking

Cast irons generally have less susceptibility to SCC due to their fabrication process which limits stresses in the material compared to other processes. However, cast irons still exhibit SCC in a number of environments. The flake graphite structure, found in gray irons and high silicon irons have been found to be more susceptible than other cast irons in the presence acid environments. The acids diffuse into the iron along graphite boundaries and the corrosive byproducts eventually produce enough pressure to crack the iron. Environments found to increase SCC in cast irons include the following:[82]

- Sodium hydroxide solutions
- Calcium nitrite solutions
- Ammonium nitrate solutions
- Sodium nitrate solutions
- Mercuric nitrate solutions
- Hydrogen sulfide solutions

- Oleum (fuming hydrogen sulfide)
- Mixed acids
- Hydrogen cyanide solutions
- Seawater
- Molten sodium-lead alloys
- Acid chloride solutions

6.12.3 Corrosion Resistance in Various Environments

Cast irons find many applications in various environments, and are selected based upon the anticipated chemicals present. Unalloyed and low-alloy cast irons corrosion rates are increased by exposure to sulfur dioxide and similar industrial type atmospheres. They are also readily attacked by chlorides, typical in marine environments. In soils, increased rates of corrosion can be expected in poorly drained areas and where corrosive chemicals are present. The addition of ~3% nickel has been used to increase corrosion resistance of cast irons in poorly drained soils. The corrosion of unalloyed cast irons in water is lower for hard water conditions, where a protective scale of calcium carbonate will develop. Protective scales do not develop well in soft and deionized waters for unalloyed cast irons, resulting in some expected corrosion. Lower pH levels will increase the rate of attack while higher pH levels reduce corrosive effects. High alloy cast irons are not typically used in these environments as their increased cost versus performance does not warrant their use. High-nickel austenitic cast irons have been used for their resistance to pitting in calm seawater conditions. High-silicon cast irons have been used for anodic protection in seawater and brackish water environments.

Cast irons also find applications in many of the common acid and alkali solutions used. They are generally attacked more in mineral acids than the organic acids. The cast irons find uses for varying concentration levels and temperatures, but impurities present can severely degrade their corrosion resistance. The resistance to mineral acids is summarized in Table 79. Unalloyed and low-alloyed cast irons have fair resistance to alkali solutions, but should be kept below 80ºC and 70% concentrations and are highly susceptible to hot solutions of ≥30% concentration levels. The addition of 3-5% nickel increases corrosion resistance to alkali solutions. The high-silicon cast irons have generally the same corrosion resistance as the unalloyed cast irons. They may be used only when impurities are present which reduce the resistance of the unalloyed irons. High-chromium cast irons are more susceptible to alkali solutions and are therefore not recommended.

Table 79   Cast Iron Acid Resistance Properties

Cast Iron	Environment
Unalloyed, low-alloyed	H_2SO_4: Limited to low-velocity, low-temperature concentrated acid (>70%) HNO_3: Limited to low-velocity, low-temperature concentrated acid. Rapid corrosion occurs in dilute to medium concentration at any temperature. HCl: Unsuitable in any concentration. H_3PO_4: May be used for concentrated solutions only, although the presence of fluorides, chlorides, or sulfuric acid will significantly reduce corrosion resistance.
High-nickel austenitic	H_2SO_4: Acceptable for room temperature and slightly elevated service in all concentrations HNO_3: Limited to low-velocity, low-temperature concentrated acid. Rapid corrosion occurs in dilute to medium concentration at any temperature. HCl: Some resistance at room temperature and below. H_3PO_4: May be used for all concentration levels and for slightly elevated temperatures. The presence of impurities will significantly reduce corrosion resistance.
High-silicon	H_2SO_4: Best resistance among cast irons. Resistant at all concentrations up to boiling. Rapidly attacked by SO_3. Slow initial passivation results in rapid attack for the first couple days, after which a slow steady corrosion rate develops. HNO_3: Good resistance to all concentrations and temperatures except dilute hot acids HCl: Best resistance among cast irons. With ~4-5% Cr, suitable for all concentrations up to 28ºC. Higher Si content with Cr and Mo can increase temperature service. However, at acid concentrations >20%, Oxidizers will attack the alloy. Initial rapid corrosion occurs for the first couple days, after which a slow steady corrosion rate develops. H_3PO_4: good resistance to all concentration levels and temperatures. The presence of fluorides makes this cast iron unacceptable for use.
High chromium	HNO_3: >20% Cr addition has good resistance, especially for dilute acids. Attacked by high temperature solutions. HCl: Unsuitable for any concentrations H_3PO_4: generally acceptable up to a 60% concentration level

6.12.4 Corrosion Protection of Cast Irons

Metal, organic, conversion, and enamel coatings are used to protect unalloyed and low-alloyed cast irons. High-alloyed irons are rarely coated. Metal coatings may be anodic to iron, providing a sacrificial protection, while other metals may be barrier type coatings. The remaining coating material types are all barrier coatings. The various coatings and applicable environments are listed in Table 80.

Table 80   Coating Materials for Cast Irons[82]

Coating Material Class	Coating Material	Environmental Application
Metals	Zinc	Rural and arid atmospheres
	Cadmium	Rural and arid atmospheres
	Tin	Food handling equipment
	Aluminum	Corrosives of sulfur fumes, organic acids, salts, nitrate-phosphate compounds
	Lead and lead-tin	H_2SO_4 and H_2SO_3
	Nickel-phosphorus	Barrier coating reaching corrosion resistance levels of stainless steels
Organics	Corrosion preventive compounds	Atmospheric protection
	Rubber-based (chlorinated neoprene and hypalon)	Used for their mechanical properties
	Bituminous paints	Water environments (low permeability coating)
	Asphaltic compounds	Alkalis, waste water, acids, tap water
	Thermosets and thermoplastics	Fluids
	Fluorocarbons	Industrial service to 205°C.
Conversion Coatings	Phosphates	Sheltered atmospheric protection
	Oxides	Sheltered atmospheric protection
	Chromates	Sheltered atmospheric protection, sometimes used with cadmium plating
Inorganic	Enamels	Acids except HF

6.13 Tin

Tin is commonly used as a coating for metals (tin plate) to provide corrosion resistance. It is a relatively inert metal that is ductile and has a low strength, which degrades significantly with increasing temperature.

Oxygen or other oxidizers readily attack tin, but it has an excellent resistance to water having a high purity, and a good resistance to salt solutions and water containing carbon dioxide. A good resistance to atmospheric corrosion is also characteristic of tin. Tin is resistant to weak acids, but is very susceptible to corrosion in alkalis, strong acids and oxidizing acids. Tin is particularly susceptible to sulfuric, hydrochloric and nitric acids.

6.14 Cadmium

Cadmium is used mostly as an electroplated coating, especially on high-strength steels in aircraft, since it improves the resistance to corrosion fatigue. It has a favorable resistance to alkalis, but is susceptible to hydrogen embrittlement.

6.15 Lead and Its Alloys

In general, lead has a very good resistance to corrosion in a number of environments including atmospheric, aqueous, and other chemical environments. Atmospheric corrosion poses almost no threat to lead due to its excellent resistance to corrosion in most types of atmospheric environments including those containing industrial pollutants (e.g. SO_2, SO_3, CO_2, H_2S, etc.). Lead's inherent corrosion resistance is mostly due to the protective film on its surface, which can form in a wide variety of environments including those containing oxides, sulfates, carbonates, and chromates. An added benefit of this film is that it is insoluble in the corrosive medium in which it is formed, which consequently results in long-term protection in that environment.

Lead is generally resistant to corrosion in fresh water and seawater, except in those water environments containing dissolved oxygen. In soil, lead also typically has a good resistance to corrosion. The presence of organic acids in the soil from wood, usually results in an increased rate of attack. Acetic, nitric and formic acids attack lead readily, but it has a good resistance to sulfuric, sulfurous, chromic and phosphoric acids and adequate resistance to hydrochloric and hydrofluoric acids. The presence of oxygen in acidic and soft water environments causes a significant increase in the corrosion rate. In the presence of most alkaline environments, lead only has a fair resistance to corrosion. Table 81 lists a number of corrosive media and lead's corresponding resistance to corrosion.

Lead is a very ductile metal with low strength and hardness properties, and due to its softness, it is especially susceptible to erosion corrosion. The corrosion resistance of lead does not vary much between the pure form and its alloys. Therefore, alloys are commonly chosen over pure lead based solely on strength properties. For instance, lead with 3-18% antimony has twice the strength of pure lead, but the strength does decrease rapidly with temperature.

6.16 Noble Metals

The corrosion resistance of the noble metals is considered excellent although there are some discrepancies in corrosion testing results of these materials. A practical upper limit on the uniform corrosion rates of noble metals is generally set at about 2 mils/yr due to their high costs. Some of the corrosion rates in various environments may extend higher than this "acceptable" limit as will be discussed. The high cost of the noble metals limits their use in functional devices to small scale applications such as electrical contacts due to their good conductivity and corrosion resistant linings where the combination of their properties make them cost effective.

Table 81   Resistance of Lead to Specific Corroding Agents[83]

Corrosive Agent	Resistance	Corrosive Agent	Resistance
Acetone	**Resistant**	Benzol	**Resistant**
Acetylene	**Resistant**	Bromine	**Resistant**
Acid, acetic	**Moderate general attack**	Carbon dioxide	**Resistant**
Acid, chromic	**Resistant**	Carbon tetrachloride	**Resistant**
Acid, citric	**Moderate general attack**	Chlorine	**Resistant**
Acid, hydrochloric	**Moderate general attack**	Dyestuffs	**Generally resistant**
Acid, hydrofluoric	**Resistant**	Formaldehyde	**Moderate general attack**
Acids, mixed	**Resistant**	Magnesium chloride	**Severe general attack**
Acid, nitric	**Severe general attack**	Magnesium sulfate	**Resistant**
Acid, phosphoric	**Resistant**	Motor fuel	**Resistant**
Acid, sulfuric	**Resistant**	Nickel sulfate	**Resistant**
Acid sulfurous	**Resistant**	Oxygen	**Resistant**
Acid, tartaric	**Moderate general attack**	Phenols	**Resistant**
Air	**Resistant**	Photographic solutions	**Generally resistant**
Alcohol, ethyl	**Resistant**	Sodium carbonate	**Resistant**
Alcohol, methyl	**Resistant**	Sodium chloride	**Resistant**
Ammonium sulfate	**Resistant**	Sodium hydroxide	**Resistant**
Ammonia	**Resistant**	Sodium Sulfate	**Resistant**
Ammonium azide	**Resistant**	Sulfur dioxide	**Resistant**
Ammonium chloride	**Resistant**	Water, chlorinated	**Resistant**
Ammonium hydroxide	**Resistant**	Water, sea	**Resistant**
Ammonium phosphate	**Resistant**		

6.16.1 Silver

Silver is a ductile material, easily processed, with good corrosion resistance making it applicable as a coating material for corrosion protection in some environments. It is used throughout the food and pharmaceutical industries for lining processing equipment as it maintains the products purity without imparting a metallic flavor to the product.[84]

Low alloying is done to improve the mechanical properties and has little effect on the corrosion resistance of silver. Sterling silver contains $\geq 92.5\%$ Ag with some Cu addition. The copper addition results in a duplex structure for most sterling silvers which can be a source of galvanic attack in strong electrolyte environments. The copper can also be selectively oxidized in elevated temperature environments. The corrosion resistance of silver in various environments is listed in Table 82.

Table 82   Susceptibility of Silver to Various Acids[84]

Environment	Corrosion Resistance
HCl	May be used under ambient conditions, but can be attacked under strong aerating conditions especially with high HCl concentrations and increased temperatures.
HI	Only should be used at room temperature with dilute HI.
HNO$_x$	Attacked by nitric and nitrous acids
H$_2$SO$_4$	Attacked by 95% concentrations at room temperature and hot (~60%) concentrations.
Cl, Br	Resistant to chlorine and bromine
I, F	Attacked by iodine and fluorine unless cathodically protected

6.16.2 Gold

The high cost of gold in combination with its susceptibility to corrosion from halogens severely limits its use for corrosion properties. Gold is readily attacked by hot mixtures of HNO$_3$ and H$_2$SO$_4$, aqua regia, hydrogen cyanide, mixtures of HBr, HCl, HI, and HNO$_3$. Gold has been used as an autoclave lining for handling phosphate mixtures up to 500ºC and in the chemical industry for lining equipment used in hydrochlorinations and hydrofluorinations.

6.16.3 Platinum

Platinum has excellent corrosion resistance properties including resistance to industrial type atmospheres containing sulfur compounds. Like other noble metals, platinum finds uses as electrical contacts and for lining process equipment. Alloying platinum with rhodium, iridium, and ruthenium slightly increase corrosion resistance. A 10% rhodium addition increases the susceptibility of platinum to corrosion from dilute HCl at slightly elevated temperatures. Alloying with palladium has essentially no effect on the corrosion resistance while large additions of silver and gold will degrade corrosion resistance to certain chemicals. Platinum is more apt to be used as an alloying element to other materials such as titanium increasing their resistance to some acids. Table 83 gives the general corrosion susceptibilities of platinum to various chemicals.

Table 83   Chemicals that Attack Platinum[84]

Chemical	Resistance
Aqua regia	Readily attacked
HBr, HI	Attacked at room temperature and increasing with elevated temperatures
HCl	Attacked by 36% HCl at 100ºC
HNO$_3$	Attacked by 70% HNO$_3$ at room temperature

6.16.4 Palladium

Palladium is similarly used as other noble metals in electrical contact and as a coating in process equipment. Palladium has been extensively researched as an alloying element to titanium as well as other metals to increase corrosion resistance to acids such as HCl, HNO$_3$, and FeCl$_3$ salts.

Palladium is generally resistant to single acids and alkalis, and to most salt solutions. The susceptibilities of Pd are to the following compounds:[84]

- Nitric acid, hydroiodic acid
- $FeCl_3$ and hypochlorite solutions
- Iodine (very slightly)
- Potassium cyanide

- Hot sulfuric acid
- Chlorine and bromine
- Aqua regia
-

6.16.5 Ruthenium

Applications of ruthenium are limited due to the difficulty in producing wrought forms. Ruthenium is used as an alloying element to platinum and palladium as a hardening agent and to titanium for corrosion resistance. It has excellent resistance to acids at room temperature and at 100ºC, including aqua regia. Chlorine, bromine, and iodine solutions will attack ruthenium.

6.16.6 Rhodium

Rhodium is primarily used as an alloying element to palladium, platinum, and nickel. It hardens these materials as well as providing increased corrosion resistance. Platinum containing rhodium is used in crucibles, furnace windings, thermocouples, and oxidation catalysts for HNO_3 and ammonia production. Thin coatings of rhodium have been used on glass to produce high reflectivity mirrors and gray filters. Rhodium is slowly attacked by sodium hypochlorite solutions at room temperature but is resistant to most all other solutions including aqua regia and concentrated acids. At 100ºC, it is attacked by sulfuric and bromic acids.

6.16.7 Osmium

Osmium is the rarest of the noble metals with a worldwide annual production usually in the range of a few thousand ounces.[84] It is alloyed in conjunction with ruthenium to other noble metals for use in electrical contacts, non-rusting pivots for small instruments, and fountain pen tips. Osmium's corrosion resistance is lower than most other noble metal, being attacked by halogens, some salt solutions, and hot acids. Osmium powder will slowly oxidize at room temperature to form osmium tetroxide.

6.16.8 Iridium

Iridium may be fabricated using conventional powder metallurgy techniques, although it is primarily used as an alloying element. Pure iridium is used in high performance spark plugs and very high temperature crucibles for single crystal preparation. It is used as a hardener and for increased corrosion resistance when added to palladium and platinum. Iridium containing 30% platinum have been used in chemical handling equipment for extremely corrosive materials and for electrical contacts in severe environments. Iridium is the most corrosion resistant metal known. It is highly resistant to virtually all acids at room temperature and at 100ºC. Iridium is slightly attacked by fused sodium, potassium hydroxides, fused sodium bicarbonate, and aqueous potassium cyanide. It has the highest resistance of the noble metals to halogen compounds, with a measured susceptibility only to moist bromine. Iridium can be dissolved in a hot aqua regia solution.

7.0 Corrosion Protection and Control Methods

Even with the proper selection of base metals and well-designed systems or structures, there is no absolute way to eliminate all corrosion. Therefore, corrosion protection methods are used to additionally mitigate and control the effects of corrosion. Corrosion protection can be in a number of different forms/strategies with perhaps multiple methods applied in severe environments. Forms of corrosion protection include the use of inhibitors, surface treatments, coatings and sealants, cathodic protection, and anodic protection. This section discusses many of the various forms of corrosion protection methods.

7.1 Inhibitors

Inhibitors are chemicals that react with the surface of a material decreasing the material's corrosion rate, or interact with the operating environment to reduce its corrosivity. Inhibitors may be introduced into the environment in which the material is operating as solutions or dispersions to form a protective film. For instance, they can be injected into a completely aqueous recirculating system (e.g. automobile radiators) to reduce the corrosion rate in that system. They may also be used as additives in coating products, such as surface treatments, primers, sealants, hard coatings, and corrosion preventive compounds (CPCs). Furthermore, some inhibitors can be added to water that is used to wash a vehicle, system or component.

Corrosion inhibitors interact with the metal, slowing the corrosion process by:

- shifting the corrosion potential of the metal's surface toward either the cathodic or anodic end
- preventing permeation of ions into the metal
- increasing the electrical resistance of the surface

The corrosion potential of a metal is shifted toward the anodic end by inhibiting the cathodic process. This is accomplished by using chemicals that inhibit the corrosion reactions taking place at the cathodic site of the corrosion cell, for example, blocking the hydrogen ions at the metal's surface from combining to form hydrogen gas. Likewise, the corrosion potential of a metal is shifted toward the cathodic end by inhibiting the anodic process. This is accomplished by using chemicals that inhibit the corrosion reactions taking place at the anodic site of the corrosion cell for example, by keeping the metal from dissociating into ions.

Preventing the permeation of ions into the metal is accomplished by forming a protective film or layer on the metal surface. Inhibitors can form a protective barrier film, which effectively isolates the metal from the corrosive environment, or they can induce the formation of precipitates that block the corrosive agents from accessing the metal. Inhibitors can also increase the electrical resistance of the metal by passivating the surface.

Inhibitors are usually grouped into five different categories: passivating, cathodic, organic, precipitation, and vapor phase. Each of these groups is discussed separately in the following sections.

7.1.1   Passivating Inhibitors

Passivating inhibitors are the most common type of inhibitors mainly because they are very effective in reducing the rate of corrosion. They protect the material by aiding in the formation of a thin, inert film on the surface of a metal, thereby moving its corrosion potential toward the noble region, which effectively passivates the metal. This shift in corrosion potential can be significant, and sometimes on the order of a 100 mV.[3] Passivating inhibitors can be either oxidizing, which do not require oxygen to be present, or nonoxidizing, which do require oxygen to be present in the environment. Oxidizing inhibitors include nitrites and nitrates, and chromates were one of the most widely used inhibitors. Although chromate inhibitors are some of the most effective, they are currently being phased out by regulations from the Environmental Protection Agency in the United States due to health and environmental concerns. Nonoxidizing inhibitors include phosphates and molybdates. These can only be used for applications which encounter oxygen-containing environments. The primary disadvantage to passivating inhibitors is that they can actually accelerate localized corrosion on the material being protected if the concentration of inhibitors falls below a critical concentration. Therefore it may be necessary to periodically reapply the corrosion inhibitor or monitor the inhibitor concentration.[10]

7.1.2   Cathodic Inhibitors

Cathodic inhibitors specifically target the cathodic region of the metal or electrochemical cell and provide protection by inhibiting the rate of the cathodic reaction. This is generally accomplished by building a barrier layer to obstruct the corrosive agents from accessing the metal surface or by preventing the reagents in the cathodic process from forming their normal products (e.g. hydrogen gas). For example, certain inhibitors can precipitate on selected cathodic areas of the metal to form a barrier, effectively isolating the metal from the environment. Also, other inhibitors can preemptively occupy or react with hydrogen or oxygen, for example, and keep them from forming hydrogen gas or, in the case of oxygen, keep it from oxidizing the metal. Calcium bicarbonate, zinc compounds, and polyphosphates are some examples of cathodic inhibitors.

7.1.3   Organic Inhibitors

Unlike cathodic inhibitors, organic inhibitors tend be active over the entire metal by adsorbing to the surface to form a thin, water-displacing film. The strength of the adsorptive bond between the metal and the film is a key factor in determining the level of protection the inhibitor will provide. This bonding strength is primarily dependent on the relative ionic charge between the metallic surface and the organic inhibitor. Anionic inhibitors (inhibitors with a negative ionic charge), such as sulfonates, are used for positively charged metal. Cationic inhibitors (inhibitors with a positive ionic charge), such as amines, are used for a negatively charged metal.[10]

7.1.4   Precipitation Inhibitors

Precipitation inhibitors are chemicals that can induce the formation of precipitates on a metal. The precipitates tend to cover the entire surface of the metal and act as somewhat of a barrier to the corrosive environment. Examples of precipitation inhibitors are silicates (e.g. sodium silicate) and phosphates.[10]

7.1.5   Vapor Phase Inhibitors

Vapor phase inhibitors are also known as volatile corrosion inhibitors are carried by a vapor phase product, such as water vapor, to the surface of the metal to be protected. When it reaches the metal surface it the vapor phase condenses, causing a release of the inhibitor ions.

7.1.6   Inhibitor Compounds

Inhibitors may be inorganic or organic materials. Inorganic inhibitors are usually crystalline salts including sodium chromates, phosphates and molybdates. The negative ions of these materials are responsible for reducing corrosion. Organic inhibitors include sodium sulfonates, phosphonates, mercaptobenzotriazole (MBT), and aliphatic or aromatic compounds containing positively charged amine groups. Inhibitors may be produced into liquids, solids including hard and soft materials, or vapors to be used in numerous applications. Their greatest use comes in systems involved with liquid heating or cooling systems. Inhibitors are introduced into the liquid media and the concentration and/or the corrosion rate of the system monitored to maintain an optimal concentration level. Vapor phase inhibitors including morpholine and hydrazine are introduced into steam environments such as boilers, to increase the pH level in the system. The selection of inhibitors will depend upon the metal requiring protection, as well as the operating environment. Various inhibitors used to protect metals in some environments are listed in Table 84.

7.2   Surface Treatments

A surface treatment is the modification of a material's surface using various means to improve some characteristic of the material, in this case the corrosion resistance. Conversion coatings and anodizing involves a chemical reaction to create an improved corrosion resistant oxide film layer on the metal's surface. Shot peening is a mechanical process to induce compressive residual stresses improving resistance to SCC and corrosion fatigue. Laser treatment uses heat to modify surface structure, aid a chemical reaction in modifying the surface, or to induce compressive residual stresses within a metal to increase its resistance to SCC and corrosion fatigue.

7.2.1   Conversion Coatings

Conversion coatings are used as a protective, or sometimes decorative, coating which is produced in-situ by a chemical reaction of a metal's surface with a chosen environment. The two main groups of conversion coatings are phosphate and chromate conversion coatings, and are discussed specifically in Section 7.3.2.

7.2.2   Anodizing

Anodizing is an electrochemical process, most frequently used on aluminum, although it can be used with other metals, such as magnesium and titanium alloys. An electric current is passed through an electrolyte (usually chromic, phosphoric, or sulfuric acid) causing the surface of the anodic metal to form an oxide film. This film can be significantly thicker than the naturally occurring one, and thus can provide better corrosion protection. An advantage of anodizing over coating deposition methods is that the resultant coating is an integral part of the substrate rather

than being a layer that is bonded to the substrate. Anodized coatings are, however, typically brittle and susceptible to strong acids and bases.

Table 84   Some Inhibitors Used to Protect Various Systems/Metals[6]

System	Inhibitor	Metal	Concentration
Acids			
HCl	Ethylaniline	Fe	0.5%
	MBT		1%
	Pyridine + phenylhydrazine		0.5% + 0.5%
	Rosin amine + ethylene oxide		0.2%
H_2SO_4	Phenylacridine		0.5%
H_3PO_4	NaI		200 pm
Others	Thiourea		1%
	Sulfonated castor oil		0.5–1.0%
	As_2O_3		0.5%
	Na_3AsO_4		0.5%
Waters			
Potable	$Ca(HCO_3)_2$	Steel, cast iron	10 ppm
	Polyphosphate	Fe, Zn, Cu, Al	5–10 ppm
	$Ca(OH)_2$	Fe, Zn, Cu	10 ppm
	Na_2SiO_3		10-20 ppm
Cooling	$Ca(HCO_3)_2$	Steel, cast iron	10 ppm
	Na_2CrO_4	Fe, Zn, Cu	0.1%
	$NaNO_2$	Fe	0.05%
	NaH_2PO_4		1%
	Morpholine		0.2%
Boilers	NaH_2PO_4	Fe, Zn, Cu	10 ppm
	Polyphosphate		10 ppm
	Morpholine	Fe	Variable
	Hydrazine		O_2 scavenger
	Ammonia		Neutralizer
	Octadecylamine		Variable
Engine Coolants	Na_2CrO_4	Fe, Pb, Cu, Zn	0.1-1%
	$NaNO_2$	Fe	0.1-1%
	Borax		1%
Glycol/water	Borax + MBT	All	1% + 0.1%
Oil field brines	Na_2SiO_3	Fe	0.01%
	Quarternairies		10-25 ppm
	Imidazoline		10-25 ppm
Seawater	Na_2SiO_3	Zn	10 ppm
	$NaNO_2$	Fe	0.5%
	$Ca(HCO_3)_2$	All	pH dependent
	$NaH_2PO_4 + NaNO_2$	Fe	10 ppm + 0.5%

7.2.3   Shot Peening

Shot peening is a cold working process originally implemented to increase fatigue strength. A stream of shot is used to bombard a metal's surface, inducing compressive stresses and relieving tensile stresses within the material.[85] The depth of the shot peening effect is typically about 0.13 to 0.25 mm below the surface. The altering of residual stresses on the metal's surface results in a higher fatigue resistant material, and also a higher resistance to corrosion fatigue and stress corrosion cracking.

7.2.4   Laser Treatment

There a four uses of laser technology to modify the surface properties of metals. One method is to harden the surface using laser heating which enhances thermal diffusion at the surface.[86] A second technique is to use laser heating to melt the surface which is then rapidly quenched to modify the surface structure. A third method uses a laser to melt the surface and alloying elements are added to the surface melt effectively creating a different material at the surface. The fourth method makes use of a laser's shock effect to induce compressive stresses within a metal's surface.[87] This has the same effect as shot peening with the major difference that it can produce residual compressive stresses to a depth of approximately 1.0 mm, resulting in higher fatigue lives. This method is referred to as "laser peening" or "laser shock processing."

7.3   Coatings and Sealants

Metallic, inorganic and organic coatings are used frequently for providing long-term corrosion protection of metals in various types of corrosive media. There are two main types of coatings: barrier coatings and sacrificial coatings. A barrier coating acts as a shield and protects the metal from the surrounding environment, whereas a sacrificial coating functions as a sacrificial anode (see Section 7.4) and thus, corrodes preferentially. Barrier coatings are typically unreactive, resistant to corrosion, and protective against wear. Sacrificial coatings provide cathodic protection by supplying electrons to the base metal. Sealants provide corrosion protection by completely securing the component from moisture penetration.

7.3.1   Metallic

Metallic coatings provide enhanced corrosion resistance of metals as either barrier coatings or sacrificial coatings. They are durable, usually easy to form, but sometimes porous, which can result in accelerated corrosion of the substrate metal. Some of the common metals used as coatings are nickel, lead, zinc, copper, cadmium, tin, chromium, and aluminum. Methods for applying metallic coatings include cladding, electrodeposition (electroplating), electroless plating, spraying, hot dipping, diffusion, chemical vapor deposition (CVD), and ion vapor deposition.

7.3.1.1   Nickel

Nickel is used as a coating for corrosion protection applications, and is also used as an undercoat for other coatings. Electrodeposition is the common method for applying nickel, but electroless plating can also be used. When nickel is used as a coating for steel, copper is sometimes used as an intermediate layer. Nickel is also used as an intermediate layer between steel and

microcracked chromium to prevent the corrosion of steel. Nickel-phosphorous coatings have a superior corrosion resistance compared to nickel coatings, and can be electrodeposited or electrolessly deposited.

7.3.1.2   Aluminum

Hot-dipping, spraying, cementation, and ion vapor deposition processes are used to deposit aluminum coatings on steel. Hot-dipped aluminum coatings are used to protect the metal substrate from atmospheric corrosion and oxidation at elevated temperatures. Sprayed aluminum coatings are sometimes sealed with organic coatings to provide more uniform and impermeable protection. Ion vapor deposited aluminum coatings are soft and formable. Aluminum coatings have a minimum thickness of approximately 8-25 μm.[6]

7.3.1.3   Lead

Electrodeposition and hot dipping are usually employed to apply lead coatings on steel, with tin sometimes added to improve bonding. Of course, lead compounds are toxic and therefore, the use of lead coatings is limited.

7.3.1.4   Copper

Copper is susceptible to atmospheric corrosion, and thus, it is not very useful as a protective coating when used alone. It is, however, useful when used in conjunction with subsequent coatings, as it has a low porosity and can work as a barrier coating with porous, corrosion resistant coating to protect the base metal from corrosion. In addition corrosion inhibitors, such as benzotriazole, can also improve the performance of copper coatings.[88]

7.3.1.5   Cadmium

Cadmium is usually a preferred coating for the corrosion protection of steel in moist and marine environments; it is anodic to steel and therefore, will act as a sacrificial anode on steel. Cadmium coatings are smooth and conductive, and resist fretting and fatigue, but have been known to cause solid metal embrittlement of steel and titanium and exfoliation of susceptible aluminum alloys. Furthermore, the corrosion products of cadmium are toxic, so it should be avoided in applications that may contaminate the environment. There are alternatives to cadmium coatings however, such as zinc and tin coatings. Cadmium coatings are applied mostly by the electrodeposition process and are good for electrical applications. Minimum coating thickness is approximately 5 – 25 μm.[6]

7.3.1.6   Zinc

Galvanization denotes the application of a zinc coating to the surface of a metal by any method. Hot dipping, electrodeposition, and spraying are a few methods used to galvanize a metal. Zinc is less expensive than cadmium, and is generally the preferred coating in industrial environments.

7.3.1.7   Chromium

Chromium coatings are hard and provide good wear resistance, but are typically used in conjunction with other coatings such as copper and nickel for corrosion protection applications.

7.3.1.8   Tin

Tin is another very common material used in coating applications and it provides good corrosion resistance to the metal substrates, either as a barrier or sacrificial coating. It is often used to coat steel and sometimes copper. Tin coatings are typically thin and porous; therefore, to achieve corrosion protection they should act as a sacrificial coating. Tin coatings are widely used in the food industry as coatings on steel containers.

7.3.1.9   Gold

Gold is often coated over other coatings to provide enhanced appearance or improved electrical properties. Gold coatings are used mostly for electrical applications (and jewelry) as they have a low contact resistance.

7.3.2   Ceramic

Ceramic coatings are inorganic, nonmetallic coatings that act as a barrier between the corrosive environment and the base material being protected. They often consist of an oxide film that is formed on the surface of a metal by chemical reaction, which can occur naturally on some metals; however, more effective corrosion resistant coatings can be produced. Ceramic coatings are especially useful for providing high temperature corrosion protection. Examples of ceramic coatings include chromate films and phosphate coatings.

7.3.2.1   Chromate Films

Although chromate films provide a significant improvement in the corrosion resistance of a metal substrate, it is mainly used as a precursor to other coatings and paints. Chromate coatings are often used on steel, copper, aluminum, magnesium, nickel, silver, tin, and cadmium substrates.[89] Thin chromate films can be applied by immersion, spraying, or brushing.

7.3.2.2   Phosphate Films

Metal phosphate coatings, which form on the surface of a metal when subjected to the appropriate environment by chemical reaction, are used mainly for corrosion protection, but in addition, they provide a good surface for other coatings to adhere to. When combined with corrosion inhibitors or other coatings, the corrosion protection is improved significantly. Phosphate coatings are usually applied either by spraying for larger components or by immersion in solution baths. Immersion is the preferred method as a more homogeneous coating is produced.

7.3.3   Organic

Organic coatings are widely used for corrosion protection applications on exterior surfaces and also for interior coatings and linings. In fact, organic coatings are used more for corrosion

protection than any other protection method available; they can also provide enhanced appearance of a previously dull or unattractive metal. There are several types of organic coatings, which include paints, varnishes, enamels, and lacquers, and numerous organic materials to choose from for corrosion protection applications. The types of coatings are defined below in Table 85.

Table 85   Organic Coating Types and Definitions[9]

Coating Type	Definition
Paint	A pigmented composition of liquid consistency which after application as a thin layer is converted to solid, adherent, tough film.
Oil Paint	A paint that contains drying oil or oil varnish as the basic film-forming vehicle
Water Paint	A paint that contains a water emulsion or dispersion as the basic ingredient
Enamel	A paint that is characterized by an especially smooth surface film.
Varnish	A liquid composition which after application as a thin layer is converted to a transparent or translucent solid film. Varnish is generally a clear liquid combining a drying oil and a fortifying resin, air-drying by oxidation of the oil.
Lacquer	A film-forming liquid composition containing polymeric esters or ethers and plasticizers as the basic film-forming ingredients in a solvent, and which dries by evaporation of the solvent. Lacquer may be constituted with or without resins.
Baking Finish	A paint or varnish that requires baking above 66 °C (150 °F) for the development of the desired properties.

Organic coatings have three basic methods of protecting a metal substrate from corrosion: 1) by preventing the attacking agents from penetrating through to the metal (impermeability), 2) by inhibiting attacking agents, and 3) by functioning as a cathodically protective material. An impermeable coating will protect the metallic substrate from having to face otherwise harmful environments that contain corrosive agents. Organic coatings containing inhibitors can neutralize the attacking corrosive agents by reacting with them and possibly forming a protective film on the metallic substrate. Cathodically protective organic coatings contain additives which decreases the corrosion potential between the metal and the surrounding corrosive environment.

An organic coating system will often have three components: 1) a primer, 2) an intermediate coat, and 3) a topcoat. The primer is very important to the integrity of the coating system. It is the fundamental layer of the system and thus provides the basic adhesion between the metal substrate and the intermediate or subsequent layer of the coating system, as well as corrosion protection. The intermediate coat provides corrosion resistance and thickness to the coating system. The top-coat is also very important since it provides the first level of protection against corrosion and acts as a seal over the intermediate coat and primer. Typically it is thinner than the priming coat, has good wear and abrasion resistance, and usually determines the appearance of the organic coating system.

Proper coating selection is clearly one of the most important aspects in protecting the metal from corrosion. There are, however, three other important factors that should be given proper consideration along with selecting the proper organic coating in order to provide the optimal service life. The first (1) is surface preparation, which is important for providing a strong bond between the coating and the substrate. The second (2) is proper selection and application of a priming coat, which should have good adherence to the substrate and should be compatible with

the coating. Poor adhesion or incompatibility could lead to coating failure. The third (3) important factor is the proper selection of a topcoat; however, the topcoat is unimportant if the surface is prepared poorly or an improper primer is selected since the coating will fail anyway.

The ingredients of organic coatings usually include volatile and non-volatile components. The volatile components serve as thinners, while the non-volatile components act as the film-forming ingredients (e.g. resin, oil, wax etc.) and sometimes include pigments and plasticizers.[9] The pigments have several functions; they provide protection against moisture penetration, resist corrosion, protect against sunlight, and add consistency and color to the coating. Plasticizers are used to keep the coating from cracking.

Organic coatings have some advantages and disadvantages when compared to metallic coatings.[9] For instance, they are usually more economical, can be applied on top of metallic and inorganic coatings, come in various colors and have a broad range of physical characteristics. They are, however, more susceptible to mechanical damage, and they don't offer any anodic protection to areas of the substrate that are exposed.

Table 86 provides a summary of various organic materials used in coating systems. The table shows the advantages and disadvantages of the different resin materials, including properties and characteristics, compatibility with other materials, as well as their performance and compatibility in certain environments.

Table 86   Advantages and Limitations of Principal Organic Coating Materials[90]

Resin Type	Advantages	Limitations	Comments
Alkyds	Good resistance to atmospheric weathering and moderate chemical fumes; not resistant to chemical splash and spillage. Long oil alkyds have good penetration but are slow drying; short oil alkyds are fast drying. Temperature resistant to 105 °C (225 °F)	Not chemically resistant; not suitable for application over alkaline surfaces, such as fresh concrete or for water immersion.	Long oil alkyds make excellent primers for rusted and pitted steel and wooden surfaces. Corrosion resistance is adequate for mild chemical fumes that predominate in many industrial areas. Used as interior and exterior industrial and marine finishes.
Epoxy esters	Good weather resistance; chemical resistance better than alkyds and usually sufficient to resist normal atmospheric corrosive attack	Generally the least resistant epoxy resin. Not resistant to strong chemical fumes, splash or spillage. Temperature resistance: 105 °C (225 °F) in dry atmospheres. Not suitable for immersion service	A high quality oil-base coating with good compatibility with most other coating types. Easy to apply. Used widely for atmospheric resistance in chemical environments on structural steel, tank exteriors, etc.
Vinyls	Insoluble in oils, greases, aliphatic hydrocarbons, and alcohols. Resistant to water and salt solutions. Not attacked at room temperature by inorganic acids and alkalis. Fire resistant: good abrasion resistance.	Strong polar solvents redissolve the vinyl. Initial adhesion poor. Relatively low thickness (0.04 to 0.05 mm, or 1.5 to 2 mils) per cost. Some types will not adhere to bare steel without primer. Pinholes in dried film are more prevalent than in other coating types.	Tough and flexible, low toxicity, tasteless, colorless, fire resistant. Used in potable water tanks and sanitary equipment; widely used industrial coating. May not comply with Volatile Organic Compound (VOC) regulations.

Table 86, continued - Advantages and Limitations of Principal Organic Coating Materials

Resin Type	Advantages	Limitations	Comments
Chlorinated rubbers	Low moisture permeability and excellent resistance to water. Resistant to strong acids, alkalis, bleaches, soaps and detergents, mineral oils, mold, and mildew. Good abrasion resistance.	Redissolved in strong solvents. Degraded by heat (95 °C, or 200 °F, dry; 60 °C or 140 °F wet) and ultraviolet light, but can be stabilized to improve these properties. May be difficult to spray, especially in hot weather.	Fire resistant, odorless, tasteless, and nontoxic. Quick drying and excellent adhesion to concrete and steel. Used in concrete and masonry paints, swimming pool coatings, industrial coatings, marine finishes.
Coal tar pitch	Excellent water resistance (greater than all other types of coatings); good resistance to acids, alkalis, and mineral, animal, and vegetable oils.	Unless cross linked with another resin, is thermoplastic and will flow at temperatures of 40 °C (100 °F) or less. Hardens and embrittles in cold weather. Black color only will alligator and crack upon prolonged sunlight exposure, although still protective.	Used as moisture-resistant coatings in immersion and underground service. Widely used as pipeline exterior and interior coatings below grade. Pitch emulsions used as pavement sealers. Relatively inexpensive.
Polyamide-cured epoxies	Superior to amine-cured epoxies for water resistance. Excellent adhesion, gloss, hardness impact, and abrasion resistance. More flexible and tougher than amine-cured epoxies. Temperature resistance: 105 °C (225 °F) dry; 65 °C (150 °F) wet.	Cross linking does not occur below 5 °C (40 °F). Maximum resistances generally require 7-day cure at 20 °C (70 °F). Slightly lower chemical resistance than amine-cured epoxies.	Easier to apply and topcoat, more flexible, and better moisture resistance than amine-cured epoxies. Excellent adhesion over steel and concrete. A widely used industrial and marine maintenance coating. Some formulations can be applied to wet or underwater surfaces.
Coal tar epoxies	Excellent resistance to saltwater and freshwater immersion. Very good acid and alkali resistance. Solvent resistance is good, although immersion in strong solvents may leach the coal tar.	Embrittles upon exposure to cold or ultraviolet light. Cold weather abrasion resistance is poor. Should be topcoated within 48 h to avoid intercoat adhesion problems. Will not cure below 10 °C (50 °F). Black or dark colors only. Temperature resistance: 105 °C (225 °F) dry; 65 °C (150 °F) wet.	Good water resistance. Thicknesses to 0.25 mm (10 mils) per coat. Can be applied to bare steel or concrete without a primer. Low cost per unit coverage.
Polyurethanes (aromatic or aliphatic)	Aliphatic urethanes are noted for their chemically excellent gloss, color, and ultraviolet light resistance. Properties vary widely, depending on the polyol coreactant. Generally, chemical and moisture resistances are similar to those of polyamide-cured epoxies, and abrasion resistance is usually excellent.	Because of the versatility of the isocyanate reaction, wide diversity exists in specific coating properties. Exposure to the isocyanate should be minimized to avoid sensitivity that may result in an asthmatic-like breathing condition upon continued exposure. Carbon dioxide is released upon exposure to humidity, which may result in gassing or bubbling of the coating in humid conditions Aromatic urethanes may darken or yellow upon exposure to ultraviolet radiation	Aliphatic urethanes are widely used as glossy light-fast topcoats on many exterior structures in corrosive environments. They are relatively expensive, but extremely durable. The isocyanate can be combined with other generic materials to enhance chemical, moisture, low-temperature, and abrasion resistance.

Table 86, continued - Advantages and Limitations of Principal Organic Coating Materials

Resin Type	Advantages	Limitations	Comments
Asphalt pitch	Good water resistance and ultraviolet stability. Will not crack or degrade in sunlight. Nontoxic and suitable for exposure to food products. Resistant to mineral salts and alkalis to 30 % concentration.	Black color only. Poor resistance to hydrocarbon solvents, oils, fats and some organic solvents. Do not have the moisture resistance of coal tars. Can embrittle after prolonged exposure to dry environments or temperatures above 150 °C (300 °F), and can soften and flow at temperatures as low as 40 °C (100 °F).	Often used as relatively inexpensive coating in atmospheric service, where coal tars cannot be used. Relatively inexpensive. Most common use is as a pavement sealer or roof coating.
Water emulsion latex	Resistant to water, mild chemical fumes, and weathering. Good alkali resistance. Latexes are compatible with most generic coating types, either as an undercoat or topcoat.	Must be stored above freezing. Does not penetrate chalky surfaces. Exterior weather and chemical resistance not as good as solvent or oil-base coatings. Not suitable for immersion service.	Ease of application and cleanup. No toxic solvents. Good concrete and masonry sealers because breathing film allows passage of water vapor. Used as interior and exterior coatings.
Acrylics	Excellent light and ultraviolet stability, gloss, and color retention. Good chemical resistance and excellent atmospheric weathering resistance. Resistant to chemical fumes and occasional mild chemical splash and spillage. Minimal chalking, little if any darkening upon prolonged exposure to ultraviolet light.	Thermoplastic and water emulsion acrylics not suitable for any immersion service or any substantial acid or alkaline chemical exposure. Most acrylic coatings are used as topcoats in atmospheric service. Acrylic emulsions have limitations described under "Water emulsion latex."	Used predominantly where light stability, gloss, and color retention are of primary importance. With cross linking, greater chemical resistance can be achieved. Cross-linked acrylics are the most common automotive finish. Emulsion acrylics are often used as primers on concrete block and masonry surfaces. Also useful for protecting aluminum alloys and other non-ferrous alloys.
Amine-cured epoxies	Excellent resistance to alkalis, most organic and inorganic acids, water, and aqueous salt solutions. Solvent resistance and resistance to oxidizing agents are good as long as not continually wetted. Amine adducts (formed by an addition reaction) have slightly less chemical and moisture resistance.	Harder and less flexible than other epoxies and intolerant of moisture during application. Coating will chalk on exposure to ultraviolet light. Strong solvents may lift coatings. Temperature resistance: 105 °C (225 °F) wet; 90 °C (190 °F) dry. Will not cure below 5°C (40 °F); should be topcoated within 72 h to avoid intercoat delamination. Maximum properties require curing time of about 7 days.	Good chemical and weather resistance. Best chemical resistance of epoxy family. Excellent adhesion to steel and concrete. Widely used in maintenance coatings and tank linings.
Phenolics	Greatest solvent resistance of all organic coatings described. Excellent resistance to aliphatic and aromatic hydrocarbons, alcohols, esters, ethers, ketones, and chlorinated solvents. Wet temperature resistance to 95 °C (200 °F). Odorless, tasteless, and nontoxic; suitable for food use.	Must be baked at a metal temperature ranging from 175 to 230 °C (350 to 450 °F). Coating must be applied in a thin film (approximately 0.025 mm or 1 mil) and partially baked between coats. Multiple thin coats are necessary to allow water from the condensation reaction to be removed. Cured coating is difficult to patch due to extreme solvent resistance. Poor resistance to alkalis and strong oxidants.	A brown color results upon baking, which can be used to indicate the degree of cross linking. Widely used as tank lining for alcohol storage and fermentation and other food products. Used for hot water immersion service. Can be modified with epoxies and other resins to enhance water, chemical, and heat resistance.

Table 86, continued - Advantages and Limitations of Principal Organic Coating Materials

Resin Type	Advantages	Limitations	Comments
Organic zinc-rich	Galvanic protection afforded by the zinc content, with chemical moisture resistance similar to that of the organic binder.	Generally have lower service performance than inorganic zinc – rich coatings, but ease of application and surface preparation tolerance make them increasingly popular.	Widely used in Europe and the Far East, while inorganic zinc-rich coatings are most common in North America. Organic binder can be closely tailored to topcoats (for example, epoxy topcoats over epoxy-zinc-rich coatings) for a more compatible system. Organic zinc-rich coatings are often used to repair galvanized or inorganic zinc-rich coatings.
Inorganic zinc-rich	Provides excellent long-term protection against pitting in neutral and near-neutral atmospheric, and some immersion, services. Abrasion resistance is excellent, and dry heat resistance exceeds 370 °C (700 °F). Water-base inorganic silicates are available for confined and VOC compliance.	Inorganic nature necessitates thorough blast-cleaning surface preparation and results in difficulty when topcoating with organic topcoats. Zinc dust is reactive outside the pH range of 5-10, and topcoating is necessary in chemical fume environments. Somewhat difficult to apply; may mudcrack (irregular fracture formed by shrinkage caused by drying) at thicknesses in excess of 0.13 mm (5 mils).	Ethyl silicate zinc-rich coatings require atmospheric moisture to cure and are the most common type. Widely used as a primer on bridges, offshore structures, and steel in the building and chemical-processing industries. Used as a weldable preconstruction primer in the automotive and shipbuilding industries. Use eliminates pitting corrosion.

7.3.3.1   Corrosion Preventive Compounds (CPCs)

The organic coating system is typically expected to be a longer-term protection method for metals, but there are temporary protective organic materials that can provide short-term protection against corrosion. These are called corrosion preventive compounds (CPCs). CPCs are generally separated into two categories: water displacing and non-water displacing compounds. They are often used on places where the protective coating has been damaged and the metal substrate is exposed until the coating can be reapplied. CPCs can be used on both interior and exterior surfaces for corrosion protection. Although some CPCs may appear to be a permanent film, they can usually be removed with an appropriate solvent, and are not expected to be a long-term solution to corrosion.

The water displacing compounds are usually clear or translucent, soft, oily compounds, however some form hard, dry films. These can fill cracks and crevices and form a thin protective layer that is less than 1 mm thick.[91] Non-water displacing compounds are typically thick, colored, and can be either hard or soft and are usually used for longer periods than the water displacing compounds. Generally, CPCs are applied as fluids by wiping, brushing, spraying or dipping.[6]

Three of the most common CPCs are described in military specifications. These are MIL-C-16173, MIL-C-81309, and MIL-C-85054. MIL-C-16173 is a soft, water-displacing CPC that is sprayed on as a brown film. MIL-C-81309 is a very thin compound which forms a soft film after drying. MIL-C-85054, which is also known as Amlguard, forms a hard, clear film after drying and is of the most commonly used CPCs due to its superior protection capability. Some of the more common CPCs are categorized in Table 87.

Table 87   List of Some Common CPCs[10]

Water Displacing (Soft)	Water Displacing (Hard)	Non-Water Displacing (Soft)	Non-Water Displacing (Hard)
ACF-50	AV-8	Fluid Film NAS	Ardrox 3322
Ardrox 3107	AMLGUARD (AML-350)	LPS-3 Heavy Duty Inhibitor	Dinol AV-30
Ardrox 3961	Cor-Ban 35		Dinol AV-40
Boeshield T-9	VCI-368		LPS Procyon
Cor-Ban 22			ZipChem ZC-029
CorrosionX			
CRC Protector 100			
CRC 3-36			
Dinitrol AV8			
Mobilarma 245			
LPS-2			
LPS-3			
WD40			

7.3.3.2   Rubber

Rubber is not like most other organic coatings, since it is usually used as a lining material on pipes or tanks. They provide an excellent resistance to water.

7.3.4   Coating Processes

There are a number of methods, ranging from simple to sophisticated, that are used to apply coatings, and there are advantages and disadvantages to each method. The quality of the application of a coating is critical because any defect or significant porosity in the coating can result in severe localized corrosion. Selection of a coating application method is usually based on the type of coating (i.e. metallic, ceramic, organic), the type of substrate to be coated, the amount of surface area that will be coated, and whether there are any environmental regulations or restrictions. Application methods for metallic coatings include cladding, electrodeposition (electroplating), flame spraying, vapor deposition, and hot dipping. Application methods for ceramic coatings include diffusion, spraying, and chemical conversion.[12] Application methods for organic coatings include brushing, rolling, and spraying. Materials and application methods of metallic, inorganic, and organic coatings will be described below.

7.3.4.1   Hot-Dipping

Hot dipping designates the coating application process of immersing a metal substrate in a molten metal bath, which is usually aluminum, zinc, tin, or lead. Since the applied coating consists of a molten metal, the melting temperature of the metal coating should be relatively low. Hot dipping can be either a continuous or batch process. Hot-dip galvanizing is the most common metal coating method; it involves the application of a thin layer of zinc to carbon steel. The zinc layer provides cathodic protection of the steel thereby protecting the steel from corrosion. Figure 66 shows the service life of hot-dip galvanized steel in different environments.
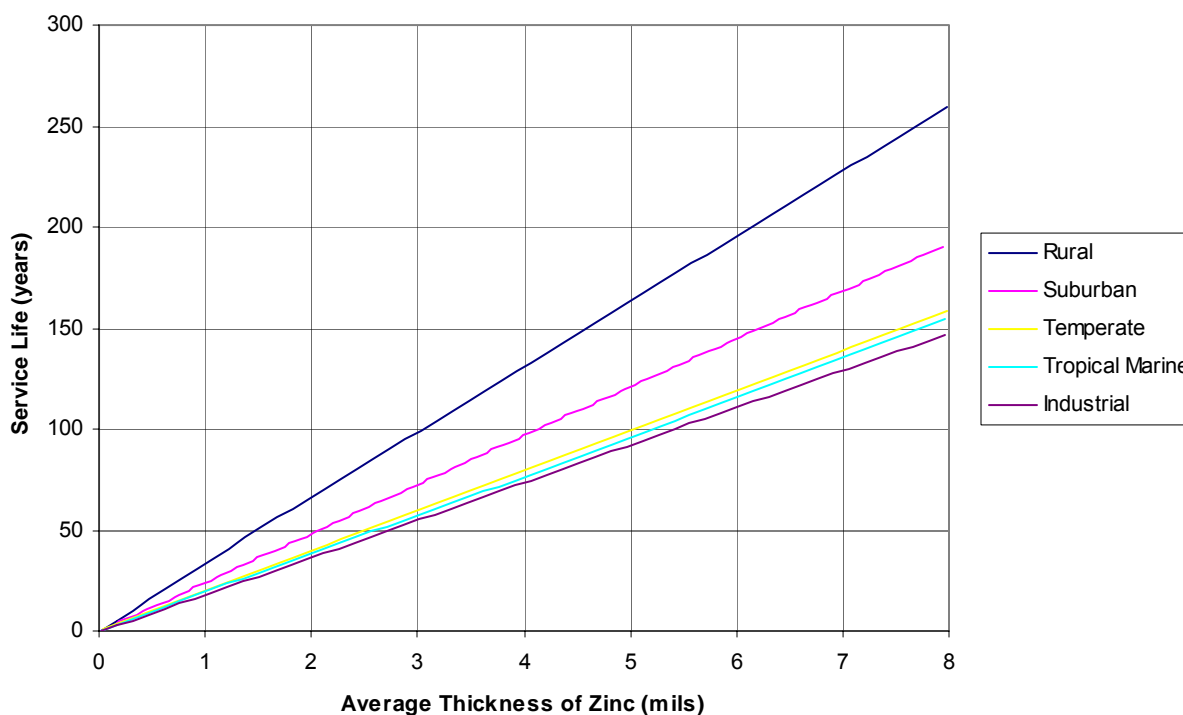
Figure 66   Service Life[2] for Hot-Dip Galvanized Coatings[92]

7.3.4.2   Electrodeposition

Electrodeposition, also called electroplating, is a process where a thin metal layer is deposited on a metal substrate in order to enhance the surface properties, including its corrosion resistance. The metal substrate is placed in an electrolytic solution containing dissolved metal ions, which will ultimately become the coating. An electrical current is passed through the solution, between two electrodes, causing the ions to deposit on the cathode (metal substrate) resulting in a metallic coating.

Characteristics of the coating are dependent on control of the processing parameters including temperature, current density, residence time and composition of the solution.[12] The physical and mechanical properties of these coatings can be altered by varying the processing parameters. They can be made to be thick or thin, hard or soft, or have a layered composition.

A variety of metals are available for use as electrodeposited coatings and include aluminum, chromium, iron, cobalt, nickel, copper, zinc, rhodium, palladium, silver, cadmium, indium, tin, rhenium, platinum, gold, lead, brass, bronze and a number of other alloys. As with all coating application methods, electrodeposition has its advantages and disadvantages.

7.3.4.3   Electroless Plating

Electroless nickel plating is similar to the electrodeposition process except that it does not require an external electrical current to be applied. It is a chemical reduction process where

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[2] Service Life is defined as the time to 5% corrosion of the steel surface

nickel ions are driven to the surface of the substrate metal by a reducing agent which is also present in the host solution. If processing conditions are properly maintained and the composition of the aqueous solution is uniform, the deposition of the nickel should be uniform over the entire surface of the substrate, even if it has a complex geometry.

7.3.4.4   Cladding

Metal claddings typically provide corrosion protection by acting as a barrier and a sacrificial coating. The cladding method involves a thin metal layer that is installed on the metal substrate by pressing, rolling or extrusion. This produces a metal layer with essentially zero porosity. An advantage is that this allows a thin piece of expensive, corrosion resistant material to be used on an inexpensive thicker piece of metal that is susceptible to corrosion instead of using the corrosion resistant material as the entire piece.

7.3.4.5   Thermal Spraying

Thermal spraying is a coating process in which a material feed is melted by a flame and sprayed by compressed gas onto a substrate; when the molten droplets/particles hit the substrate they flatten and adhere to the surface to form a coating. The process involves the build-up of these flattened particles which melt to form a cohesive coating that adheres to the substrate and covers the entire surface, while filling irregularities on the surface. Bonding between the coating and substrate usually results from mechanical interlock or diffusion and alloying. Therefore, surface preparation of the substrate is an important aspect in the quality of the coating. Often, it is required for the surface to be roughened in order to promote good mechanical adhesion between the coating and substrate. Thermal spraying can be performed using flame spraying, electric arc, or plasma arc.

7.3.4.6   Physical Vapor Deposition

There are several coating application methods which are subsets of the physical vapor deposition category. These include sputtering, evaporation, and ion plating. PVD processes involve plasma bombardment to deposit the metal over the entire area of the substrate.

7.3.4.7   Sputtering

Sputtering is the process where a target material is bombarded by gas ions causing atoms to be ejected and consequently deposited onto the substrate. Some advantages and disadvantages of this process are given in Table 88.

7.3.4.8   Evaporation

Evaporation is a relatively simple process that involves the vaporization of a metal, which is subsequently deposited on a substrate. The adhesion of coatings deposited by this method is only marginal and uniformity is difficult to achieve. Therefore, the evaporation method is not typically used for corrosion prevention applications.

7.3.4.9   Ion Plating

Ion plating is a process in which ions are driven from a plasma by an electrical bias on the substrate where they are deposited. Alternatively, the coating can be applied using an ion beam deposition technique, where plasma ions bombard the substrate to create nucleation sites for a neutral ion species. The neutral species can then deposit onto the nucleation sites, resulting in the formation of a coating.

7.3.4.10   Laser Surface Alloying

Laser surface alloying involves feeding the metal to be deposited into a laser beam. The laser beam melts the metal and deposits it on the surface of the substrate, where heat is transferred and a strong metallurgical bond is formed.

7.3.4.11   CVD

Chemical vapor deposition processes involve coating a substrate by chemical means, namely by reacting a precursor gas on the metal substrate. The gas is mixed in a chamber causing it to become reactive and is then sent to another chamber to be deposited onto the substrate. The gas mixture reacts at the surface of the substrate, which is heated in order to drive the endothermic reaction, to ultimately form the coating. It is important in this process to maintain a non-contaminated system. Table 88 lists some of the advantages and disadvantages corresponding to the various coating application methods.

7.3.4.12   Brushing

Brushing is perhaps the most intuitive coating application process, and is used to apply organic based coatings. It is a manual application method, and there are numerous types of brushes that can be used. It is very important to select the appropriate type of brush with the proper bristles in order to produce a high quality coating. The brush size, shape, and bristle type are all important considerations when selecting a brush for a specific coating application. This is because poor brush selection can lead to uneven or discontinuous coating application, runs, drips, or other unfavorable coating characteristics. A standard wall brush is often used for applying coatings to structural steel or similar surfaces. Oval-shaped brushes are used for other structural and marine applications, and are also used to apply coatings near rivets, boltheads, piping, railings and other difficult to reach areas.[64]

Brushes are made with either synthetic, typically nylon, or natural fibers for bristles. The advantage to using a brush with synthetic bristles is that it has a very good resistance to abrasion and are good to use on rough surfaces such. Brushes with synthetic bristles are also less expensive than those employing natural fibers. One of the primary disadvantages to synthetic bristles is that they may be susceptible to strong solvents such as ketones. Natural bristles are more expensive and sensitive to water, but they have a good resistance to strong solvents and are capable of a much finer, uniform coating application.[64]

An advantage to the application method of brushing is the ability to perform what's called striping. Striping is used to apply the coating around irregular areas that cannot be easily or properly coated through a spraying or other coating technique. Areas that typically require striping include edges, rivets, fasteners, corners, boltheads, and welds. It is a recommended

procedure because it can provide the proper coating thickness around these irregular areas, which would not be able to be achieved otherwise. Striping is not used, however, for coatings that have a solute that must remain in suspension, such as zinc-rich coatings. The brushing application method can also achieve complete coating penetration in particularly porous surface areas on a substrate.[64]

A disadvantage of the brushing application method is that it is time consuming as opposed to the spraying methods. Also when applied over a large surface area it is very difficult to maintain a uniform coating thickness through brushing, and therefore it is not a practical method for components or systems with large areas. Furthermore, after the coating dries the surface may have brush marks or slight grooves left over from the bristles. This usually is only a detriment to the appearance rather than the functionality. Another disadvantage to using the brushing method is that it is a difficult technique to use for coatings containing a high solid content and also for fast drying coatings.[64]

Brushing is most commonly used for applying oil-based or water-based coatings to surfaces with small or irregular areas. There are proper techniques in applying the coating that give the best results in the end product. Either an experienced professional or a well-trained technician should be used to apply coatings on critical assets or components.[64]

7.3.4.13 Rolling

Rolling is another manual coating application process, and it requires a roller assembly consisting of a core roller and a cover to absorb and apply the coating material. The assembly can vary in diameter as well as length, and there are also various cover materials. Common cover materials are polyester, nylon, mohair, and lambskin. Of course, the cover material is usually selected to suit the type of surface to be coated.[64]

There are three types of roller cores: pipe rollers, fence rollers, and pressure rollers. Pipe rollers are used just as the name suggests: for coating surfaces such as pipes. The surfaces usually are contoured and need the roller to flex and cover the surface. Fence rollers use roller covers that have an extra long fiber length, which enables them to simultaneously coat both sides of a surface such as fence wire. Pressure rollers are more sophisticated and have a feed line that moves the coating material to the inside of the roller core from a pressurized tank. The core is a porous material which allows the coating to pass through to the surface of the cover, and thus pressure rollers can provide continuous application of the coating.[64]

Rolling is a good application method for coating large, flat surfaces. A disadvantage is that it is much more difficult to achieve coating penetration into porous or cracked surfaces using the rolling coating application method, and is therefore not recommended for rough or irregular surfaces. Rolling does provide a fine quality finished surface on smooth surfaces. Rolling is a faster process than brushing, but is slower than other coating methods such as spraying.[64]

The roller coating application method is typically used to apply oil-based and water-based coatings, and can also be used to apply epoxy and urethane coatings. This method is not recommended for applying coatings containing a high solids content, zinc rich coatings, or high performance coatings and linings. As with the brushing application method there are proper techniques that result in uniform and quality application of the coating on the substrate.[64]

7.3.4.14   Spraying

There are several variations of the spray coating application method, including high volume-low pressure spraying, airless spray, air-assisted airless spray, plural component spray, and electrostatic spray. Conventional spraying simply uses compressed air to atomize coating particles and propel them toward the substrate. Though simple, the efficiency with which the coating successfully reaches the intended surface is low: ~ 25-30%. Conventional spraying is used to apply coatings such as latex paints, lacquers, stains, sealers, zinc-rich mixtures, alkyds, and epoxies.[64]

An advantage of the spray application technique is that it requires significantly less time than brushing and rolling, and therefore it can be used to coat large surface areas. It also results in a smooth, uniformly coated surface compared to brushing and rolling, and does not leave brush or speckle marks or a textured appearance. Spraying equipment can also be used to clean off the surface prior to applying the coating. Spraying can produce a high quality, smooth surface.[64]

A low efficiency for the amount of coating that is deposited on the substrate is one disadvantage to the spray application method. Spraying can be a slower process than other coating methods. It also is sometimes difficult to coat hard to reach areas, such as edges corners, and irregular surfaces with spraying. Since the equipment required for spraying is more expensive than that used for other coating methods, it must be cleaned after each use and properly maintained to ensure durability of the equipment.[64]

High volume low pressure spraying is a spraying technique that uses approximately the same amount of compressed air as conventional spraying but requires less pressure to atomize the coating material. This results in a lower velocity air/coating stream and consequently improves the transfer efficiency from ~30% to up to 70%. This effectively reduces the coating costs by preserving more coating material. The negative side of high volume low pressure spraying is that the application time needed to coat an equivalent surface area compared to conventional spraying is increased. Furthermore, this spraying technique may not be suitable for applying more viscous coatings due to the low pressure requirement.[64]

Airless spraying is another spraying technique that uses a fluid pump to pressurize and propel the coating material onto the substrate. Advantages to using this technique include good surface penetration (e.g. cracks, porous surfaces), better irregular surface coverage (e.g. corners, edges), quick film buildup, rapid area coverage, and higher viscosity coating materials. The coating material transfer efficiency is usually between 30 and 50%. One of the disadvantages to airless spraying is that it is difficult to adjust and change the equipment configurations (e.g. nozzles, orifices) while in the field. It also does not atomize the coating material as well as the conventional spraying method. Poor application techniques using this particular method can result in coating deficiencies such as solvent entrapment, voids, runs, sags, pinholes, and wrinkles.[64]

A variation of the airless spraying method is the air-assisted airless spray, which incorporates the advantages of the airless spray method and the conventional spray method. For instance, it combines the fine atomization abilities of the conventional spray with the improved production and surface penetration characteristics of the airless spray. This method allows the coating material to be joined with a compressed air jet after it has been atomized in the absence of air. This results in a further atomization of the coating material before it reaches the substrate. This combined method is useful for applying fillers, glazes, lacquers and polyurethanes.[64]

Plural component spraying is a complex application method that mixes coating components immediately before the coating is propelled to the substrate. This method is used for high-solids coatings and for coatings with a short cure time, such as epoxies. This method can be performed by any of the spraying methods mentioned above. This method is used to apply polyesters, polyurethanes, vinyl esters, and epoxies.[64]

Electrostatic spraying is also a coating application process that utilizes the various atomization methods mentioned above (i.e. conventional, airless, air assisted airless). It utilizes an electrostatic, high voltage supply to direct the atomized particles to the substrate by electrostatic attraction. This technique is used to coat irregularly shaped substrates such as cables, piping, and fencing. The advantages of this coating method are that it improves the coating material transfer efficiency, has a good rate of application, and has good atomization properties. A disadvantage to this method is that it has a tendency for non-uniform deposition of the coating near irregular shaped objects on a surface. Furthermore, it requires special formulation of the coating material.[64]

Proper application techniques are critical when using spraying techniques in order to achieve a high quality, uniform coating on the substrate. Therefore, it is very important that the applicator have either the necessary experience or training in order to produce acceptable coating results.

Table 88　　　Advantages and Disadvantages of Coating Application Methods[6, 64, 88]

Coating Method	Advantages	Disadvantages
Electrodeposition	Can choose from a variety of coatings Versatility of application – can be used on components for many different applications Common coating method Coatings are electrically conductive Can be sacrificial or barrier coating Coatings can be weldable and solderable Coating thickness can be controlled Substrate can be more formable with electrodeposited coating compared to other coating methods	▪ Color limitations ▪ Some substrates may not be receptive to coating ▪ Coating application may be limited by geometry and very large parts.
Electroless Plating	▪ Uniform deposition ▪ Low porosity ▪ Less hydrogen absorption compared to electroplated nickel and hard chrome ▪ No (or compressive) residual stress ▪ Coatings have lubricity ▪ Coatings are weldable and solderable ▪ Higher hardness than electroplated coatings	
Cladding	▪ Essentially zero porosity	▪ Limited to simple geometries
Hot Dipping	▪ Can coat difficult geometries ▪ Resistant to mechanical damage	▪ Coating metal must have relatively low melting temperature

Table 88, continued - Advantages and Disadvantages of Coating Application Methods

Coating Method	Advantages	Disadvantages
Sputtering	- Can produce thin films - Good adhesion - Highly automatic process - High quality - Uniform deposition	- Limited thickness - High cost - Difficult to coat substrate uniformly
Evaporation	Used with most metals	- Difficult to coat substrate uniformly - Adhesion is marginal
CVD	- Can deposit thick, dense films - High quality - Good Adhesion - Generally costs less than PVD	- May have residual stresses - May require high temperatures for deposition - May contain impurities - Limited number of coatings available
Thermal Spraying	- Excellent long-term corrosion resistance - Minimal maintenance - Can apply thick coatings - Excellent paintability - No heat distortion - Can apply coatings on-site	
Brushing	- Inexpensive equipment - High quality coating near irregular surface areas - Good surface penetration	- Time consuming - Difficult to maintain uniformity over large surface areas - May leave brush marks or slight grooves on surface
Rolling	- Can be used for large surface areas - Faster application compared to brushing	- Poor surface penetration - Relatively slow process - May leave speckled texture on surface
Spraying	- Faster application than brushing and rolling - Can be used for large surface areas - Results in a smooth, uniform coating - Can have good surface penetration	- Low coating transfer efficiency - Requires experienced technicians to apply coatings

7.4   Cathodic Protection

Cathodic protection (CP) is a widely used electrochemical method for protecting a structure or important components of a system from corrosion. A CP system is essentially an electrochemical cell and must have a cathode, an anode, an electrical connection between them and an electrolyte. The principle behind CP is that dissolution of a metal (cathode) can be suppressed by supplying it with electrons, and in effect, controlling the corrosion. Corrosion is then targeted on the anode instead of the metal. Since an electrolyte is required for this method of protection, CP is not effective for systems in air or other environments that resist current flow between the anode and cathode.

There are two main classes of CP: active and passive. Active cathodic protection, also called impressed-current, requires the use of an external power supply. In this type of protection, the negative terminal of the power supply is connected to the metal to be protected, and the positive terminal is connected to an inert anode. The anode, however, is often not more anodic to the metal, and can be even more cathodic than the metal. The impressed-current ensures that current flows such that the metal acts as the cathode and is therefore protected from corrosion. Moreover, the anodes are not typically consumed by corrosion in impressed-current CP systems, since they do not undergo the typical corrosion reactions. It is possible to overprotect a system using impressed-current CP. If the voltage is too high, the metal can experience hydrogen embrittlement (e.g. steel) or possibly accelerated corrosion (e.g. aluminum). Therefore, proper conditions for the system should be determined in order to optimize the protection.

Passive CP systems are simpler than impressed-current systems and involve the galvanic coupling of the metal to be protected to a sacrificial anode, which corrodes preferentially. The anode in this type of system must be more anodic than the metal and must also readily corrode without passivation in order for the system to be successful. In some instances the sacrificial anode must be replaced after it has been consumed to ensure protection of the structure. A comparison of the characteristics of the active and passive CP systems is provided in Table 89.

Table 89   Comparison between Sacrificial Anode and Impressed-Current Cathodic Protection Systems[93]

Passive Cathodic Protection	Active Cathodic Protection
Simple……………………………………	Complex
Low/no maintenance……………………….	Requires maintenance
Works best in conductive electrolytes……...	Can work in low-conductivity electrolytes
Lower installation costs for smaller installations…………………………………	Remote anodes possible
Higher capital investment for large systems.	Low capital investment for large systems
	Can cause the following problems: ▪ Stray current corrosion ▪ Hydrogen embrittlement ▪ Coating debonding ▪ Cathodic corrosion of aluminum

There are several anodes that are available for use in cathodic protection applications. For passive CP systems magnesium, aluminum and zinc are commonly used. Characteristics of some sacrificial anodes are given in Table 90. Furthermore, there is a variety of anodes available for active CP systems. These include high-silicon cast iron, graphite, polymers, precious metals, lead alloys, and ceramics. Table 91 gives a comparison of the consumption rate between various sacrificial and impressed-current anodes.

Table 90   Characteristics of Sacrificial Anodes[11]

Sacrificial Anode Type	Density (lb/in³)	Half Cell Potential vs. SCE (V)	Consumption Rate (lb/amp. yr.)	Theoretical Current Capacity (Amp. Hrs./lb)	Actual Current Capacity (Amp. Hrs/lb)	Efficiency (%)
Zinc	0.256	-1.04	25	372	355	95
Aluminum/Mercury	0.100	-1.04	6.8	1,352	1,280	95
Aluminum/Indium	0.100	-1.08	7.6	1,352	1,150	85
Aluminum/Tin	0.100	-1.05	7.4	1,352	1,176	87

Table 91   Comparison of Sacrificial and Impressed-Current Anodes for Cathodic Protection[12, 93]

Anode	Consumption Rate (lb/A-yr)
Sacrificial Anodes	
Magnesium	18
Zinc	25
Aluminum-Tin	16-20
Aluminum-Zinc-Tin	7.4-20.8
Aluminum-Zinc-Indium	8-11.5
Aluminum-Zinc-Mercury	6.8-7
Impressed-Current Anodes	
Scrap Steel	20
Aluminum	10-12
Graphite	0.25-5
High-Silicon Iron and Si-Cr Iron	0.25-1
Lead	0.1-0.25
Platinized Titanium	0
Pb-6Sb-1Ag	0.1-0.2

Impressed current cathodic protection is sometimes not practical, such as when the metal is in an extremely corrosive environment, which would require a prohibitively high current. Therefore, CP is sometimes used in conjunction with other protection methods in order to enhance the level of protection and avoiding an impractical system. It is common for pipelines, for example, to be coated with an organic coating, and CP is used to protect the structure from corrosion where there are weaknesses or defects in the coating, known as holidays.

A notable disadvantage of CP, specifically active CP, is the resulting stray-current effects it may impose on nearby systems or structures. Stray currents can be picked up by metallic components or structures that are in close proximity to the CP system, potentially resulting in accelerated corrosion of that metal component or system, as depicted in Figure 67.
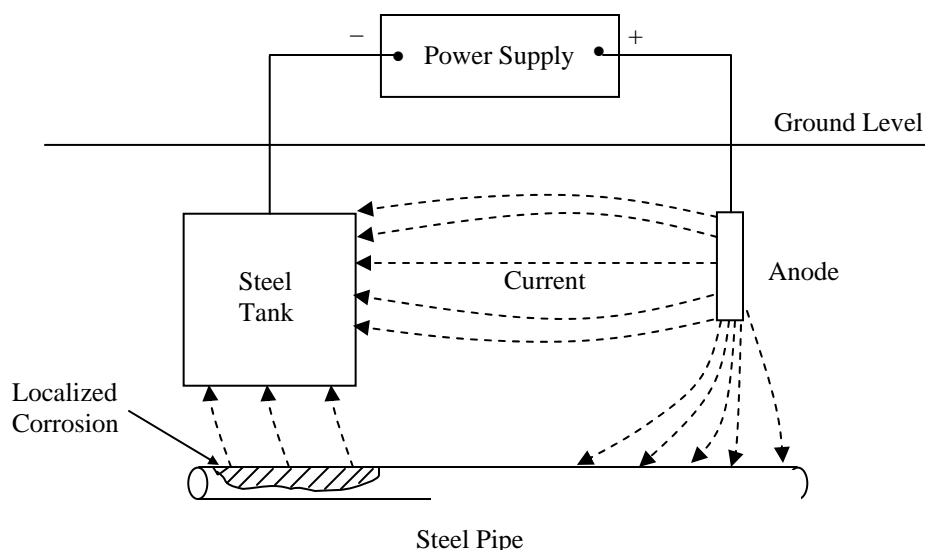
Figure 67   Stray Currents Resulting from Cathodic Protection[12]

Cathodic protection systems are usually designed and implemented by a company that specializes in this field. Choosing the right system and then designing it is not a straightforward process, and usually requires expert knowledge to determine what is best for a specific system in a specific environment. Therefore, it is generally recommended that an expert company be contracted or at least consulted to do such work.

7.5   Anodic Protection

Anodic protection is a method of corrosion control that was developed more recently than cathodic protection, but it is used less frequently. As its name implies, anodic protection shields the anodic electrode in the system from corrosion rather than the cathodic electrode as in CP. The principle behind anodic protection, however, is not quite analogous to that of CP. Essentially, instead of shifting corrosion potential from the metal to be protected to an anodic material as in CP, anodic protection involves passivation of the metal to be protected. A passive film forms on the surface of the metal with the application of an electrical current. Once this film is formed, it acts to protect the metal from dissolution, and the film itself is nearly insoluble in the environment which it formed. Passivation causes metals to become very non-reactive and consequently very resistant to corrosion. The limitation of this type of corrosion control is that not every metal can be protected this way; only certain metals in specific environments can be anodically protected. These include the metals and solutions shown in Table 92.

Table 92   Metals and Solutions Capable of Being Anodically Protected[94]

Solutions	Metals
Sulfuric acid	Steels
Phosphoric acid	Stainless steels
Nitric acid	Nickel
Nitrate solutions	Nickel alloys
Aqueous ammonia	Chromium
Organic acids	
Caustic solutions	

Anodic protection requires three electrodes, a potential controller (potentiostat), and a power source. The necessary electrodes are a cathode, a reference electrode and an anode, which is by definition the metal to be protected. The reference electrode monitors the voltage on the anode, and is very important since it is necessary to maintain proper protection and avoid accelerated corrosion. The cathode should be resistant to dissolution; it can be platinum on brass, steel, silicon cast iron, copper, stainless steel, or nickel-plated steel, among others. The potential controller actively controls the potential on the anode.

A notable advantage of anodic protection is that after the passive film has formed, the amount of current required to maintain this protective film is very small. A further advantage is that the applied current is equal to the corrosion rate of the protected metal. This allows the instantaneous corrosion rate to be measured, which is not the case for CP. Moreover, anodic protection is effective in weak and strong corrosive media. Furthermore, the operating conditions for anodic protection systems can be determined accurately by laboratory-scale experiments, whereas, to do so for CP is hardly a scientific procedure. A general comparison of anodic protection and cathodic protection methods is provided in Table 93.

Table 93   Comparison of Anodic and Cathodic Protection

	Anodic Protection	**Cathodic Protection**
Applicability		
Metals	Active-passive metals only	All metals
Corrosives	Weak – aggressive	Weak – moderate
Relative Cost		
Installation	High	Low
Operation	Very low	Medium to high
Throwing Power	Very high	Low
Significance of applied current	Often a direct measure of protected corrosion rate	Complex – does not indicate corrosion rate
Operating Conditions	Can be accurately and rapidly determined by electrochemical measurements	Must usually be determined by empirical testing

Throwing power indicates the distribution uniformity of the current density that is required. To achieve uniform protection, for example, electrodes need to be placed close together if the throwing power is low. On the other hand, if the throwing power is high, the electrodes can be placed farther apart. In anodic protection, for instance, a single cathode can protect a wider area of metal because it has a high throwing power.

8.0   Corrosion Monitoring and Inspection Technologies

There are numerous methods that may be used to monitor or inspect components for corrosion and corrosion related damage. The following section is aimed only at introducing available technologies and their applicability to the various forms of corrosion. Corrosion monitoring involves methodologies to assess the corrosivity of a system which may or may not be continuous (real-time monitoring) and to continuously monitor systems for defect formation. Corrosion inspection is the periodic checking of a system for corrosion and corrosion related defects. Since corrosion fatigue and stress corrosion cracking involves the formation and propagation of cracks, monitoring and inspection techniques to look for surface and subsurface cracks have been included.

8.1   Corrosion Monitoring

Corrosion monitoring is used to predict component wear out and to manage the corrosivity of the environment. There are a couple different methodologies used in the field of corrosion monitoring. One method uses probes (sensors) to monitor the chemical or electrochemical nature of the environment. The data collected is then used to relate to corrosion rates of materials, which is not always a direct method. Furthermore, probes can be adversely affected under certain conditions leading to erroneous corrosion rate determinations. A corrosion coupon is a second method, providing a low technology method to measure corrosion rates of materials. Acoustic emission is used to detect the formation of surface and subsurface damage in materials.

8.1.1   Coupon Testing

Coupon testing involves placing a sample within a system. The sample is removed periodically for inspection and weight loss measurements. Coupon testing is a simple procedure but is often overlooked as it is an old and low technology method. However, coupons provide the most reliable evidence, whereby information on the forms and location of corrosion on the samples, the average rate of corrosion, and the corrosion byproducts can be obtained. The downfalls are that it is time consuming and does not provide real time data.

8.1.2   Electrical Resistance Probes

Electrical resistance probes measure the change (increase) in electrical resistance due to a reduced cross-sectional area of the sensing element as a result of corrosion. The sensitivity of the sensor increases with a decrease in thickness of the sensing element; however this also results in a reduced lifetime. Any build up of deposits on the sensing element will affect the electrical resistance readings from the probe. Electrical resistance probes are also temperature dependent requiring an additional shielded probe for proper corrosion rate adjustments. They may be permanently installed within a system for continuous monitoring or potable for periodic measurements.

8.1.3   Inductive Resistance Probes

Inductive resistance probes measure a reduction in sensing element thickness by changes in the inductive resistance of a coil in the probe. By using sensing elements with a high magnetic

permeability, the magnetic field around the coil is intensified. Any change in thickness of the elements will change the magnetic field encompassing the coil, and thus the corrosion rate may be obtained. Inductive resistance probes require a temperature adjustment similar to electrical resistance probes. The sensitivity of induction resistance probes is higher than with the electrical resistance probes.

8.1.4   Linear Polarization Resistance

The linear polarization resistance (LPR) monitoring method is an electrochemical method used to measure instantaneous rates of uniform corrosion and is widely applied under full immersion aqueous environments. A small potential, about 5-20mV, is applied to a sensor electrode with the direct current being measured. The solution resistance should be measured independently and subtracted from the measured resistance for accuracy. The polarization resistance obtained is inversely proportional to the corrosion rate. This method has been used for more than thirty years in virtually all types of water-based environments.

8.1.5   Electrical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS), like LPR, uses the polarization of electrodes to measure corrosion rates. The difference is that EIS uses alternating currents and measures the resulting phase shift relative to the applied current. The applied frequency is about 0.1 Hz to 100 kHz with more than one frequency required to obtain useful data. Typically, two frequencies are used; however, full frequency measurements may be used, producing the best data to identify the corrosion processes taking place.

8.1.6   Electrochemical Noise

The electrochemical noise method measures changes in the electric potential and current between freely corroding electrodes. Highly sensitive instrumentation is required as the fluctuations are on such a small scale. Three electrodes are needed to simultaneously measure both the potential and current noise. Different corrosion processes will produce different noise signatures. This data may be used to identify pit initiation and growth before visible detection. However, the interpretation of signals is complex, with different strategies developed to help interpret results. Although this method is proven and can detect different corrosion processes, there is skepticism over the accuracy of corrosion rates derived from the measurements.

8.1.7   Zero Resistance Ammetry

Zero resistance ammetry is the measure of galvanic currents between two materials. This is accomplished by placing samples of the materials into a sensor unit, which is placed in the system environment. Deviation from actual component materials may occur due to slight differences in composition, heat treatment, surface condition and applied stresses. This technique can be used to monitor changes to the environment by using the same material for both sensor elements.

8.1.8   Thin Layer Activation

Thin layer activation involves inducing radioactive species on the surface layer of a material, and subsequently measuring gamma ray emission to determine the corrosion rate. A high energy

beam of charged particles is used to bombard a material's surface, producing radioactive elements in the surface area. One example is the formation of Co^{56} within steel. This isotope will decay into Fe^{56}, emitting gamma rays in the process. The change in gamma ray emission is used to determine the rate of material loss. A radioactive surface may be induced on system components or sample materials to be placed within the system.

8.1.9 Electric Field Method

This technique is used to look for corrosion across large structures by applying an electric current across the structure and measuring the resulting voltage distribution. Arrays of pins for the measurements are placed in specific areas across the structure. Increasing the distance between pins reduces the ability to detect localized corrosion. This method is widely used to detect corrosion on the interior of pipelines.

8.1.10 Corrosion Potential

Measuring the corrosion potential to determine the risk of corrosion is a direct result of corrosion kinetics (Appendix A). The corrosion potential of a material is measured relative to a reference electrode. This method is widely used to assess the corrosion of steel rebar in concrete and underground pipes incorporating cathodic protection. It is also used for structures containing anodic protection.

8.1.11 Hydrogen Probes

Hydrogen probes can be used to measure corrosion rate and to detect the diffusion of atomic hydrogen into materials. Many corrosion processes involve atomic hydrogen as a product of the corrosion reaction. Thus, by measuring the atomic hydrogen present, a corrosion rate may be determined. Hydrogen probes are more often used to detect the diffusion of atomic hydrogen into adjacent materials, such as pipe walls, as hydrogen-induced cracking may result. Hydrogen monitoring has been highly beneficial in oil refining and petrochemical industries due to the presence of hydrogen sulfide in such plants.

8.1.12 Chemical Analysis

Chemical analysis involves the inspection of materials, usually fluids, from a system for corrosion reaction by-products. This method is widely used to monitor the health of emergency generators through routine oil analysis. Particles in the waste oil are identified and quantified to monitor any abnormal wear and/or corrosion within the system.

8.1.13 Acoustic Emission

Acoustic emission is a monitoring technique where elastic waves are generated by the release of energy built up in stressed materials revealing the formation of a defect. The elastic waves must be continuously recorded for interpretation. This method is complicated by the normal emission of waves produced by thermal or mechanical stresses exhibited on the system. The interpreter must therefore be experienced to dismiss such "background noise" and diagnose abnormal events. This technique can be used to detect the formation of defects such as crack growth, material

corrosion, surface rubbing, and leaking fluids. A summary of the corrosion monitoring methods is provided in Table 94.

Table 94   Advantages and Disadvantages of Corrosion Monitoring Methods[6]

Monitoring Techniques	Advantages	Disadvantages
Corrosion Coupons	- Low cost - Many forms of corrosion may be monitored - Applicable to all corrosive environments	- Erosion and heat transfer effects not easily simulated - Long exposure times required for meaningful data collection (not real-time) - Labor intensive - Removal of coupons from the system for examination and cleaning will affect the corrosion rate if the coupon is reused.
Electrical Resistance	- mature technology with several commercial suppliers - probes do not have to be removed from the system to obtain weight loss data	- Only suitable to measure uniform corrosion - The sensitivity lacks the ability for real-time data collection with short durations going undetected. - Gives erroneous results in the presence of conductive products or deposits on the probe
Inductive Resistance	Better sensitivity and less affected by temperature changes than electrical resistivity probes.	A more recent technology with commercial products largely applicable to uniform corrosion only
Linear Polarization Resistance	The sensitivity allows real-time measurements in appropriate environments	- Based on uniform corrosion only - An environment with a relatively high ionic conductivity is required for this method - Unstable corrosion potentials will produce erroneous measurements - Electrode surface colors in long-term surface have been observed to be different than freely corroding surfaces. Idealized theoretical conditions are assumed which is not always the case in practice - Conductive species may cause short circuiting of the electrodes, producing erroneous results
Electrochemical Impedance Spectroscopy	- More suited to low-conductivity environments than DC polarization - Can provide information on the state of organic coatings - Detailed characterization of the corroding surface is possible	- The instrumentation and interpretation of results is complex - Usually limited to uniform corrosion, although may used to detect pitting corrosion in certain systems - Full frequency analysis is rarely used in the field - The corrosion potential has to be stable to obtain useful data at low frequencies - The applied potential perturbation may affect the corroding sensor element, especially for long-term, repeated use conditions.

Table 94, continued - Advantages and Disadvantages of Corrosion Monitoring Methods

Monitoring Techniques	Advantages	Disadvantages
Electrochemical Noise	- Highly sensitive and performs well under limited conductivity, such as thin-film corrosion - One of the few techniques with the ability to detect localized corrosion including pitting damage and certain submodes of stress corrosion cracking	The data analysis requirements are complex with substantial experience needed for interpreting noise signals
Zero Resistance Ammetry	Simple method to monitor galvanic corrosion and the effects of treatments to prevent it	- The measured currents may not accurately represent galvanic corrosion since it is highly dependent upon the anode: cathode area ratio - An increase in current readings is not always related to an increase in galvanic corrosion
Thin Layer Activation	- Desirable for direct measurements of actual components - Small areas may be irradiated for monitoring such as weld zones - May be used to monitor erosion corrosion	- The instrumentation used is only applicable to small components - The results are only meaningful if the radioactive species are removed from the material's surface during the corrosion process. - Low sensitivity
Electrical Field Signature Method	- Corrosion damage is monitored in actual components - Once instruments are installed, monitoring may be performed over several years with minimal maintenance	- Does not distinguish between internal and external flaws - The interpretation of voltage signals for localized corrosion is complex - Not highly sensitive, especially for small areas
Acoustic Emission	- Applicable to a wide range of materials including non-conducting ones - Monitoring may be performed over larger areas rather than at specific points of interest	- Only detects actively growing defects - Does not detect defect size - Requires a high level of skill for interpretation of results
Corrosion Potential	The method and instrumentation are relatively simple	Only an indication of corrosion behavior and not a measurement of corrosion rate
Hydrogen Probes	The attachment of probes on external surfaces for hydrogen diffusion measurements is convenient and can be easily changed	- Measurements are restricted to a small area - Restricted to systems where hydrogen is produced in the cathodic reaction - Guidelines that correlate hydrogen uptake to actual damage has not been established
Chemical Analysis	- In well characterized systems, it may be possible to perform cost effective monitoring with such techniques - Provides useful supplementary information, to the direct measurement methods, for identifying and solving corrosion problems	- Does not measure corrosion rates - Many chemical analysis methods require outside laboratory evaluations so that immediate information is not available

8.2   Corrosion Inspection

Corrosion Inspection Methods are periodic checks of materials and material systems to detect corrosion and corrosion related defects including cracks. The success of many of these methods lies with the operator and their experience with locating and identifying corrosion.   Low technology methods are limited to surface damage only. They include visual inspection, liquid penetrant inspection, and magnetic particle inspection. High technology methods are used to detect subsurface defects, damage to hidden areas, and damage too small for visual inspection. These methods usually induce some form of energy into the material of interest, such as x-rays, sound waves, or heat, and measure the absorption/reflection of the energy. The data collected is then used to "map" defects found in the material.   Experience with the various equipment/methods and second or third inspection methods may be required to identify exactly what type of defect has been detected.

8.2.1   Visual

Visual Inspection involves the observation of light reflected from the surface of an object to the human eye. Although not a highly technical method, it's the most widely used technique for corrosion inspection.   The quality of inspection is directly related to the experience of the inspector with the equipment and environmental conditions. Corrosion products are sometimes visible, which can lead to the identification of the corrosion problem.   The appearance of corrosion products from several alloys is provided in Table 95.

8.2.2   Enhanced Visual

Borescopes and fiberscopes provide a means to inspect interior areas of critical and corrosion prone components. A borescope is a thin rod shaped optical device that transmits an image from the components interior to the inspector's eye. Critical areas are designed with access ports for borescope inspections. Fiberscopes work in the same way as borescopes, but they are flexible so that a wider area may be observed. Video imaging may also be incorporated into these devices so that the images can be viewed on a video monitor.

8.2.3   Liquid Penetrant Inspection

Liquid penetrant inspections provide a low cost option for locating surface cracks too small to be seen by visual inspection. An ultraviolet reflective liquid is first sprayed or wiped onto the surface of the material. After a period of time, the liquid will enter cracks via capillary action. The excess liquid is wiped from the surface and a powder is then applied. The powder draws the liquid back out of the crevices to the surface. An ultraviolet light is then used to illuminate the surface revealing the remaining liquid. The area of the liquid will be larger than the crack size.

8.2.4   Magnetic Particle Inspection

Magnetic particle inspection is used to find surface defects in ferromagnetic materials such as steel and iron. Magnetic particles, which may be dry or suspended in a liquid and colored or fluorescent, are dispersed over the material's surface. A magnetic field is then induced in the material which produces flux lines which will be distorted by defects. Care must be taken in surface preparation as scratches and irregularities will also distort magnetic flux lines.

Table 95   Corrosion of Metals – Nature and Appearance of Corrosion Products[95]

Alloys	Type of Attack to which Alloy is Susceptible	Appearance of Corrosion Product
Aluminum Alloys	Surface pitting, intergranular and exfoliation.	White or gray powder.
Titanium Alloys	Highly corrosion resistant. Extended or repeated contact with chlorinated solvents may result in degradation of the metals structural properties.	No visible corrosion products.
Magnesium Alloys	Highly susceptible to pitting.	White powdery snow-like mounds, and white spots on surface.
Low Alloy Steels (4000-8000 series)	Surface oxidation, pitting, and intergranular.	Reddish-brown oxide (rust).
Corrosion Resistant Steel (CRES) (300-400 series)	Intergranular corrosion (due to improper heat treatment). Some tendency to pitting in marine environment (300 series more corrosion resistant than 400 series). Stress corrosion cracking.	Corrosion evidenced by rough surface; sometimes by red, brown or black stain.
Nickel-Based Alloys (Inconel)	Generally have good corrosion-resistant qualities. Sometimes susceptible to pitting.	Green powdery deposit.
Copper-Based Alloy, Brass, Bronze	Surface and intergranular corrosion.	Blue or blue-green powder deposit.
Cadmium (used as a protective plating for steel)	Good corrosion resistance. If attack occurs, will protect steel from attack.	White, powdery corrosion products.
Chromium (used as a wear-resistant plating for steels)	Subject to pitting in chloride environments.	Chromium, being cathodic to steel, does not corrode itself, but promotes rusting of steel where pits occur in the coating.

8.2.5   Eddy Current Inspection

Eddy currents are used to detect defects on and below the surface of a material. An alternating magnetic field is applied to the surface of the material. This induces eddy currents in the material producing a magnetic field which opposes the applied magnetic field. The measured impedance is used to map the defects in the material. Low frequency eddy current, roughly 100 Hz – 50 kHz, is used to penetrate deeper into a material.

8.2.6   Ultrasonic Inspection

Ultrasonic inspection uses high frequency sound waves transmitted through the material of interest. The transmitted sound wave will be reflected back to the source by both defects in the material and once the wave has reached the other side of the material. The recorded sound wave is then used to map defects in the material and also to measure the thickness of the material. The identification of defects found in a material is left up to operator experience and/or additional inspection methods. Ultrasonic inspection is costly compared with other methods requiring large equipment and operator experience.

8.2.7 Radiography

Radiography is a method whereby x-rays, gamma rays, or neutrons are transmitted into a material and the absorption data recorded is then used to find any defects within the material. Again, the identification of defects is left up to operator experience or aided with the used of additional inspection methods. Neutron radiography is the most sensitive/most costly of these techniques.

8.2.8 Thermography

Thermography is a measure of the infrared radiation a material system emits. The underlying principal is that a good mechanical bond between materials is also a good thermal bond. It may be used to detect corrosion, debonding, cracking, thinning, water absorption, among other defects. Thermography is not widely used due to its cost and limitation to surface defect detection. A comparison between various nondestructive inspection techniques is given in Table 96.

Table 96   Nondestructive Inspection Methods[3]

Technology	Advantages	Disadvantages	Primary Defects
Visual	▪ Relatively inexpensive ▪ Large area coverage ▪ Portability	▪ Highly subjective ▪ Measurements not precise ▪ Limited to surface inspection ▪ Labor intensive	Surface, exfoliation, pitting, and intergranular corrosion
Enhanced Visual	▪ Large area coverage ▪ Very fast ▪ Very sensitive to lap joint corrosion ▪ Multi-layer	▪ Quantification difficult ▪ Subjective – requires experience ▪ Requires surface preparation	Same as visual except enhanced through magnification or accessibility
Eddy Current	▪ Relatively inexpensive ▪ Good resolution ▪ Multiple layer capability ▪ Portability	▪ Low throughput ▪ Interpretation of output ▪ Operator training ▪ Human factors (tedium)	Surface and subsurface flaws such as cracks, exfoliation corrosion around fasteners and corrosion thinning
Ultrasonic	▪ Good resolution ▪ Can detect material loss and thickness	▪ Single-sided ▪ Requires couplant ▪ Cannot assess multiple layers ▪ Low throughput	Corrosion loss and delaminations, voids in laminated structures
Radiography	▪ Best resolution (~ 1%) ▪ Image interpretation	▪ Expensive ▪ Radiation safety ▪ Bulky equipment	Surface and subsurface corrosion flaws
Thermography	▪ Large area scan ▪ Relatively high throughput	▪ Complex equipment ▪ Layered structures are a problem	Surface corrosion

8.3 Corrosion Inspection Devices

Corrosion inspection devices that incorporate more than one inspection technique have been developed to improve the reliability of accurate detection of corrosion defects. These devices must be hand held for ease of use and cost effective. The two following devices have been

developed for aircraft inspections to identify cracks and hidden corrosion by scanning the device across surface areas of the aircraft.

8.3.1   Mobile Automated Ultrasonic Scanner

The Mobile Automated Ultrasonic Scanner (MAUS) incorporates ultrasonic pulse-echo, ultrasonic resonance, and eddy current technologies into one unit for nondestructive inspection. MAUS IV is the forth generation device which is portable and applicable for detecting cracks and defects in materials for various components. The MAUS was developed for aircraft inspections, especially for lap joint evaluations.

8.3.2   Magneto-Optic Eddy Current Imaging

Magneto-optic eddy current imaging (MOI) is an inspection method which measures induced eddy currents using a Faraday magneto-optic sensor and displays the measurements on a video monitor. The images may be viewed in real time or recorded. The device is small enough to be hand held and may be easily moved about to scan large areas.

APPENDIX A

9.0 Electrochemistry, Kinetics, and Thermodynamics of Typical Corrosion Processes

Corrosion is a process involving the deterioration of a material and is regulated by chemical or electrochemical reactions with the surrounding environment; consequently, it also results in a degradation of the material's properties. The corrosion process occurs spontaneously when the environmental conditions thermodynamically favor a metal to be in its oxidized state. Therefore, thermodynamics is commonly used to determine the tendency of a material to corrode. To describe the chemical process of corrosion, however, electrochemistry and kinetics are used.

9.1 Electrochemistry and Kinetics

The principles of corrosion, based on electrochemistry, can be illustrated by an electrochemical cell, as shown in Figure 68. There are four necessary elements in order for corrosion to occur:

- Anode

- Cathode

- Electrolyte

- An electrical conducting path between the anode and cathode

Since corrosion requires all four of the elements listed above, it is readily obvious that corrosion prevention or control necessitates the elimination of just one of these elements and not necessarily all four.
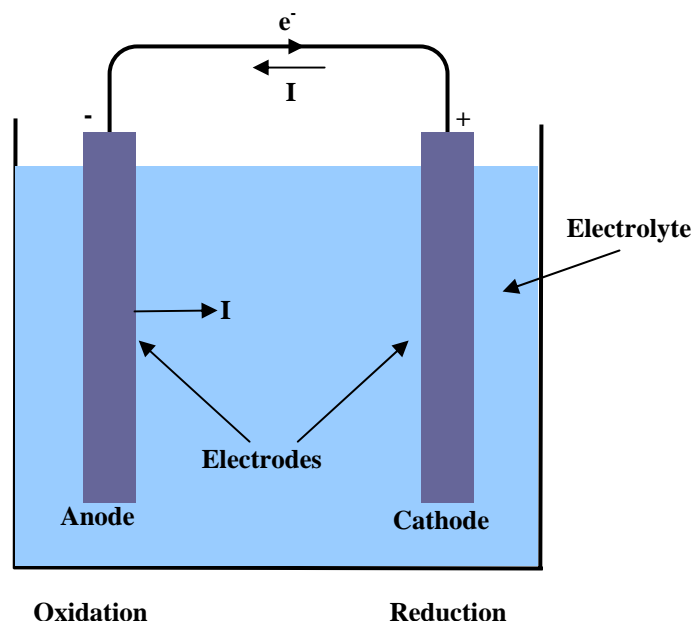

Figure 68   Electrochemical Cell Showing Principles of Corrosion

The electrochemical process of corrosion involves the transfer of electrons between the two electrodes resulting in a flow of electrical current (indicated as "I" in Figure 68), which is necessary to sustain the chemical reactions. These electrochemical reactions occur at both the anode and cathode and are oxidation-reduction reactions. The anode is host to the oxidation reaction, which generates electrons. This anodic (oxidation) reaction is described by Equation 13.

$$M \rightarrow M^{n+} + ne \qquad \text{Equation 13}$$

where

M – represents a metallic element

e – represents an electron

For the electrons to be transferred between the anode and cathode there must be an electrically conductive path, since the electrons are simultaneously consumed at the cathodic site where the reduction reaction takes place. An example of this cathodic reaction (reduction) is the evolution of a hydrogen gas from the reduction of hydrogen ions as shown in Equation 14. An example of the oxidation-reduction process is illustrated in Figure 69.

$$2H^+ + 2e \rightarrow H_2 \qquad \text{Equation 14}$$

Consumption of the electrons generated in Equation 1 could also occur by other mechanisms, as shown in Table 97.

Table 97   Other Possible Cathodic/Reduction Reactions

Metal Deposition	$M^{n+} + ne \rightarrow M$
Metal Ion Reduction	$M^{n+} + e \rightarrow M^{(n-1)+}$
Reduction of Dissolved Oxygen (Neutral or Basic Solution)	$O_2 + 2H_2O + 4e \rightarrow 4OH^-$
Reduction of Dissolved Oxygen (Acidic Solution)	$O_2 + 4H^+ + 4e \rightarrow 2H_2O$
Reduction of Water	$2H_2O + 2e \rightarrow H_2 + 2OH^-$

An electrolyte is also necessary to sustain the electrochemical reactions, given by Equation 13 and Equation 14, because it contains the ions that aid in driving the reactions. The reactions shown in Equation 13 and Equation 14 are only partial reactions, and thus, together they occur simultaneously and at the same rate.

Of course, it is not necessary to always have two distinct and separate electrodes (as shown in Figure 68) for corrosion to occur. In fact, the most common form of corrosion occurs in the presence of one metal. It is still necessary, however to have the two electrodes (i.e. the anode and the cathode). In this case, localized cells or electrodes exist on the surface of the metal, where there is a relatively small difference in electrical potential (see Figure 69). This is usually the case where there is compositional dissimilarities on the metal surface, for example, different metal phases, different crystal orientations, crystal imperfections, grain boundaries, etc.[96] An example

of this is given in the following section. Furthermore, it is not necessary that the electrolyte be in the form of a liquid. Instead, it may exist as ions in some vaporous media.

9.1.1   Example

A good example of the electrochemical corrosion process can be illustrated with the corrosion of zinc in a hydrochloric acid environment. Zinc is removed from the surface of the metal and enters the electrolytic solution in ionic form, as shown in Equation 15 and illustrated in Figure 69.

$$Zn \rightarrow Zn^{2+} + 2e \qquad\qquad \text{Equation 15}$$

Simultaneously, the two electrons released from zinc are transferred to the hydrogen ion, which is supplied from the dissociation of the acid as shown in Equation 16. Equation 14 shows the association of hydrogen ions to form hydrogen gas upon the transfer of electrons from the zinc.

$$2HCl \rightarrow 2H^+ + 2Cl^- \qquad\qquad \text{Equation 16}$$

The overall reaction of zinc with a hydrochloric acid solution can be described as in Equation 17.

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2 \qquad\qquad \text{Equation 17}$$
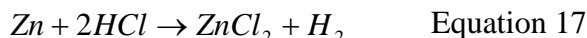
The corrosion process for other metals in like solutions is similar to that illustrated in this example; however there are other corrosion mechanisms for metals in different types of environments.
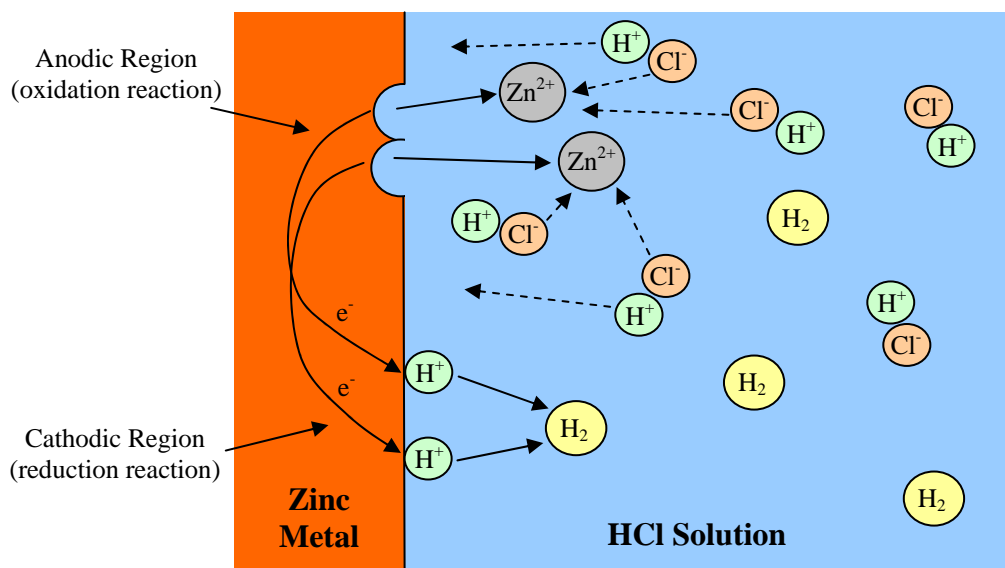
Figure 69   Illustration of the Oxidation-Reduction Process

9.2   Thermodynamics

The electrochemical reactions causing the physical corrosion of a material are spontaneous with no external driving forces, and thus, are driven only by nature's tendency to seek lower energy states, as described by the Second Law of Thermodynamics. In other words, the electrochemical reactions occur to reduce the energy in the system. The surrounding system may, however,

influence these reactions to occur at accelerated rates. For example, in an environment with an elevated temperature there is additional energy (from the heat) to drive the reactions at a faster rate. Thermodynamics, however, does not provide an indication of the rate of reaction, since it is independent of which path the reaction will take.

Thermodynamics is used primarily to determine, mathematically, the tendency for corrosion to occur, and can also be used to predict whether a metal will not experience corrosion. It cannot, however, be used to determine whether a metal will, in fact, experience corrosion or to what extent corrosion will occur.

Thermodynamics essentially quantifies the chemical stability of a system in terms of the Gibbs free energy. The amount of Gibbs free energy in a system represents the proximity of the system to equilibrium. That is, the lower the free energy, the closer the system is to equilibrium and conversely, the higher the free energy, the less stable the system is. (The free energy is at a minimum when the system is in equilibrium.) Gibbs free energy, G, at constant temperature, is given in terms of enthalpy, H, absolute temperature, T, and entropy, S as shown in Equation 18.

$$\Delta G = \Delta H - T\Delta S \qquad \text{Equation 18}$$

where

> ΔG – Change in the Gibbs free energy
> ΔH – Change in the enthalpy
> ΔS – Change in the entropy

At equilibrium, when the free energy is at a minimum, the system has no tendency to undergo chemical change, and the free energy can be represented by Equation 19.

$$\Delta G^{\circ} = -RT \ln K_{eq} \qquad \text{Equation 19}$$

where

> ΔG° – Gibbs free energy at standard state
> R – gas constant
> K_{eq} – equilibrium constant

The equilibrium constant of a reaction can be determined for a range of conditions given the standard state free energy, which is commonly available or can be determined from the free energy of formations of the products.

The potential of an electrochemical cell can be given by Equation 20, if the system is thermodynamically reversible, and if the activities of the reactants and products remain approximately constant.

$$\Delta G^{\circ} = -nFE^{\circ} \qquad \text{Equation 20}$$

where

> n – number of electrons/atom of the species involved in the reaction
> F – Faraday Constant (electric charge of 1 mole of electrons)
> E° – electrochemical cell potential at standard state

The electrochemical cell potential (E) is derived from Equation 21. The greater the difference between the electrochemical potentials of the electrodes (anode and cathode) the greater is the driving force for the corrosion reaction.

$$E = E_c - E_a \qquad \qquad \text{Equation 21}$$

where

Ec – electrochemical potential of the cathode
Ea – electrochemical potential of the anode

Combining Equation 19 and Equation 20 gives

$$\ln K_{eq} = \frac{nFE^\circ}{RT} \qquad \qquad \text{Equation 22}$$

Ultimately, Equation 22 provides the means to predict the potential of an electrochemical cell. The more negative the cell potential, the more reactive the material, and thus the material is more susceptible to corrosion. Conversely, if the cell potential is less negative or even positive, then the material is less susceptible to corrosion.

10.0   Glossary

Acetic Acid	An organic acid also known as ethanoic acid which is a carboxylic acid (CH_3COOH), and is a relatively weak acid. See also fatty acid.
Acoustic Emission	A technique where monitoring a material for the spontaneous release of sound waves is used to reveal the formation of a defect. The waves are generated from the rapid emission of waves when the material undergoes a structural change.
Acrylic Acid	An organic acid also known as propenoic acid which is an unsaturated carboxylic acid ($CH_2CHCOOH$).
Active Cathodic Protection	See Impressed-Current Cathodic Protection.
Age Hardening Steel	A form of steel which has been hardened through an aging process.
Aliphatic Compounds	A hydrocarbon compound having a straight chain of carbon atoms (i.e. alkanes, alkenes, alkynes).
Alkali	A compound or substance which has the properties of a base.
Alkaline	Having the properties of an alkali, specifically acting as a base.
Anhydrous	Absence of water.
Anion	A negatively charged ion; an ion that is attracted to the anode during an electrochemical reaction.
Anode	The positive electrode in an electrochemical cell, it attracts electrons from the cathode (anions from the electrolyte); an electrode where an oxidation reaction is taking place. Corrosion usually occurs on the anode.
Anodic Inhibitor	A chemical compound which prevents or lowers the rate of the anodic (oxidation) reaction.
Anodic Protection	A corrosion protection method that passivates the anodic element of an electrochemical cell by imposing an electric current on the anode (removing electrons from the anode) causing a passive film to form on its surface.
Anodizing	The process of chemically converting the surface of a metal by anodic oxidation to form a passive coating. Most commonly used for aluminum.
Anti-fouling	The prevention of marine organisms from growing or accumulating on the surface of a material.
Aqua Regia	"Royal Water", a highly corrosive, volatile mixture of concentrated nitric acid and hydrochloric acid with a ratio of 1 to 3, respectively. It is an extremely strong, oxidizing acid that reacts with all metals including noble metals (e.g. gold, platinum, etc.), and can dissolve all metals except for silver.
Aromatic Compounds	A hydrocarbon compound containing at least one benzene ring in its molecule, or a compound having similar chemical and physical properties to a benzene compound.
Artificial Aging	Aging process of a material that occurs above room temperature.
Atmospheric Corrosion	The gradual deterioration or alteration of a material as a consequence of being exposed to the elements constituting the atmospheric environment, such as oxygen, carbon dioxide, moisture, sulfur, and chlorine compounds.

Atmospheric Zone	The area of a material or structure that is exposed to the atmosphere.
Austenitic	A face-centered cubic structure found in ferrous materials, normally at elevated temperatures. Some ferrous metals, such as the 300 series stainless steels, exhibit this structure at ambient temperatures.
Autocatalytic Process	A catalytic process in which a product of a reaction is a catalyst for the same reaction.
Barrier Coating	A coating that, by acting as a physical barrier, prevents corrosive agents in the surrounding environment from reaching the substrate material's surface.
Beach Marks	See striation pattern
Bio-fouling	Biological fouling is the accumulation of any marine organisms or microorganisms on a material surface submerged in seawater.
Bituminous Coal Tar	A dark coal containing a high content of carbonaceous matter with 15-50% volatile matter.
Blistering	The loss of adhesion between a coating and base material causing the formation of a raised (dome-like) area, or delamination caused by the expansion or buildup of gas in a trapped area.
Borescope	A thin rod shaped optical device used for corrosion inspection that allows the interior of systems or areas inaccessible to direct viewing to be visually inspected.
Brackish Water	Water that in general contains less salt than seawater, and typically containing salt in concentrations ranging from 0.5 to 17 parts per thousand.
Brazing	A soldering process that uses the melting of a nonferrous filler metal (e.g. brass or brazing alloy), which has a lower melting point than the base metal, in order to join two metals.
Butt Joint	A joint where the two fastened metals are oriented end-to-end or edge-to-edge.
Carbide Precipitate	A chemical compound composed of carbon with one or more metallic elements, forming a second phase material, typically at grain boundaries. Most notably found in ferrous metals, but may also occur in aluminum and titanium alloys.
Carburization	The process of carbon absorption and diffusion into solid materials (typically steel) by being in physical contact with a carbonaceous material under heat, usually resulting in a higher surface hardness.
Cathode	The negative electrode in an electrochemical cell, it supplies electrons to the anode and electrolyte (attracts cations from the electrolyte); an electrode where a reduction reaction is taking place.
Cathodic Protection	A corrosion protection method that reduces the tendency of corrosion reactions to occur by supplying the metal with electrons from an external source. Two types of cathodic protection are impressed-current and sacrificial.
Cation	A positively charged ion; an ion that is attracted to the cathode during an electrochemical reaction.
Caustic Soda	A form of sodium hydroxide; it can be corrosive; it acts as a reducing agent.
Cavitation	The formation of a high concentration of vapor bubbles or cavities within a liquid, resulting in temporary localized regions of high pressure, followed by their collapse and a corresponding dramatic reduction in pressure.

Chemical Vapor Deposition A coating process that deposits a film on a substrate by reacting a precursor gas on the substrate. The gas is mixed in a chamber causing it to become reactive and is then sent to another chamber to be deposited onto the substrate. The gas mixture reacts at the surface of the substrate, which is heated in order to drive the endothermic reaction, to ultimately form the coating.

Citric Acid An organic hydroxycarboxylic acid ($HOOCCH_2C(OH)(COOH)CH_2COOH$).

Cladding A process that involves bonding a metal layer to another metal by diffusion bonding, pressing, rolling, casting, welding or extrusion.

Conversion Coating A coating that is a compound containing elements from the base metal, and is created by chemically reacting the base metal with a certain environment.

Corrodant See corrosive agent.

Corrosion The deterioration of a metal or alloy and its properties due to a chemical or electrochemical reaction with the surrounding environment.

Corrosion Cell See electrochemical cell.

Corrosion Current Density The current flowing to or from a unit area of an electrode surface during a corrosion process.

Corrosion Fatigue The failure of a material due to the combined effects of corrosion and fatigue (cyclic stressing).

Corrosion Potential The potential of a corroding surface in an electrolyte in relation to a reference electrode. The reference electrode potential is also referred to as the open-circuit potential, the rest potential, or the freely-corroding potential.

Corrosion Preventive Compound A temporary corrosion protection coating that may be a liquid, a soft solid, or a hard solid material. They are usually applied repeatedly, on a maintenance schedule, without any removal of previous coating materials, other than general cleaning of the surface.

Corrosion Rate A measure of the extent of corrosion occurring over a period of time. It is expressed in weight loss per unit time, or corrosion depth per unit time.

Corrosion Resistance A material's ability to withstand corrosion.

Corrosive Agent A chemical substance or media that corrodes a metal.

Creep Rate The time-dependent strain that occurs when under stress.

Crevice Corrosion A localized form of corrosion that occurs when an electrolyte becomes trapped and stagnant, thus setting up an electrochemical cell. This form of corrosion commonly occurs in components such as joints and those that have tight corners.

Cryogenic A term referring to very low temperatures, approaching absolute zero.

Dealloying See selective leaching

Dealuminization A specific form of selective leaching where aluminum is the element being extracted from a metal alloy.

Decarburization The process of removing carbon from the surface of a metal (commonly steel) by exposing the metal to an environment that reacts with carbon (e.g. argon-oxygen and heat).

Dezincification A specific form of selective leaching where zinc is the element being extracted from a metal alloy.

Duplex Stainless Steels Stainless steels containing chromium, nickel, and molybdenum in proportions to balance a combination of both austenite and ferrite phases.

Eddy Current Inspection	A nondestructive inspection technique used to detect defects on and below the surface of a material. This is done by applying an alternating magnetic field to the surface of the material, which induces eddy currents in the material producing a magnetic field that opposes the applied magnetic field. The measured impedance is then used to map the defects in the material.
Eddy Currents	Electrical currents produced in a material when the material is moved through a non-uniform magnetic field.
Electrical Connector	A device for connecting electrical conductors.
Electrical Impedance Spectroscopy	A nondestructive inspection technique that uses the polarization of electrodes to measure corrosion rates. This method uses alternating currents and measures the resulting phase shift relative to the applied current.
Electrochemical Cell	An electrical system composed of a cathode and anode immersed in a chemical electrolyte and produces an electromotive force through oxidation-reduction reactions. The anode and cathode may be different materials or contained within one material.
Electrochemistry	The study of chemical properties and reactions involving ions in solution.
Electrode	An electrical conductor that allows electric current to enter or leave another medium (e.g. electrolyte). It may be an electron acceptor (anode) or an electron donor (cathode).
Electrodeposition	A coating process that uses electric current to deposit metal ions from an electrolytic solution onto a substrate that acts as an electrode.
Electrogalvanizing	The electrodeposition process of coating a metal, usually steel, with zinc; it is usually performed by electroplating.
Electroless Plating	The deposition of metal ions from a solution onto a substrate, where chemical potential is the driving force.
Electrolyte	A chemical substance that conducts electricity by the migration of ions. An electrolytic substance can be a liquid, a molten compound, or sometimes a solid, containing ions.
Electrolytic Tough Pitch	Copper that has been refined electrolytically, containing mostly oxygen as an impurity.
Electroplating	A type of electrodeposition where the deposited metal is in an adherent form.
Embrittlement	The severe reduction or loss of ductility and/or toughness of a material.
End Grain	The surface of a metal where the smaller cross section of elongated grains, due to mechanical processing (e.g. drilling fastener holes), are exposed.
Enhanced Visual	An inspection technique using a borescope or fiberscope to produce visual images of interior components or areas that are inaccessible to direct viewing.
Enthalpy	A thermodynamic property describing the heat content of a system, and is defined by the sum of the internal energy of a system plus the product of the system's pressure multiplied by its volume.
Entropy	A thermodynamic property that is generally known as the measure of disorder in a system. More specifically, it is the measure of the unavailability of a system's energy to do work.
Erosion Corrosion	The increased rate of deterioration and loss of a material due to the combined effects of corrosion and the repeated motion of the surrounding environment.

Exfoliation	A form of corrosion that occurs in bands on the interior of the metal that is parallel to the metal's surface. This consequently forms corrosion products that cause a separation of the metal into layers. It is often considered a form of intergranular corrosion that attacks metals that have been mechanically treated to form elongated grain structures in one direction.
Fasteners	Fasteners are simple devices that are used to join two components or fittings and include bolts, nuts, studs and washers.
Fatigue Limit	The maximum stress that leads to fatigue fracture in a specified number of stress cycles.
Fatty Acid	An organic acid that is comprised of a hydrocarbon chain with a carboxyl group at the end ($C_nH_{2n+1}COOH$).
Faying Surfaces	The surface of a material that comes in contact with the surface of another material.
Ferritic	A body-centered cubic structure found in ferrous alloys.
Fiberscope	An optical device consisting of an arrangement of parallel glass fibers used for corrosion inspection that allows the interior of systems or areas inaccessible to direct viewing to be visually inspected.
Filiform Corrosion	A form of corrosion that exists under organic coatings on metals, blistering the coating, and is characterized by hairline resemblance.
Fish Eyes	A substance having a white crystalline appearance found on a steel fracture surface.
Fissures	A small discontinuity that resembles a crack with a slight opening of the fracture surfaces.
Flaking	see shatter cracks
Flame Spraying	A coating process where the material to be deposited is melted by an oxyfuel gas flame.
Fluids Analysis	A corrosion inspection technique where fluids are extracted from a system to look for corrosion reaction products.
Formic Acid	An organic acid also known as methanoic acid, which is the simplest form of carboxyilic acid (HCOOH).
Fretting Corrosion	A form of corrosion caused by repetitive friction between two surfaces in sliding motion with respect to each other exposed to a corrosive environment.
Fuming Nitric Acid	Concentrated nitric acid with dissolved nitrogen dioxide.
Galvanic Cell	A corrosion cell resulting from two dissimilar conducting materials being in contact with each other and in contact with an electrolyte.
Galvanic Corrosion	A form of corrosion resulting from the formation of a galvanic cell by the galvanic coupling of dissimilar metals (metals having different electrical potentials), which are exposed to an electrolyte.
Galvanic Coupling	A pair of dissimilar conductive materials that are in electrical contact.
Galvanic Series	A relative hierarchy of metals that are arranged according to their corrosion potential in a specified environment, ranging from anodic (least noble) to cathodic (most noble).
Galvanization	The process of depositing zinc onto a metal substrate such as steel. It is usually performed by hot dipping or electrogalvanizing.
General Corrosion	See uniform corrosion
Gibbs Free Energy	A thermodynamic function of enthalpy, temperature and entropy.

Grain Boundary	The disordered, or nonrepetitve atomic structure in materials surrounding the ordered (crystallographic grain) structures.
Graphitic Corrosion	A corrosion attack specific to gray cast irons whereby the corrosion process leaves behind graphite flakes (the cathodes).
Grooving Corrosion	A specialized form of corrosion that attacks electric resistance welded piping subsequently exposed to a corrosive environment. The welding process causes a redistribution of sulfides along the weld line, resulting in a preferred attack in the weld area producing grooves in the material
Halogen	A family of elements that include fluorine, chlorine, bromine, and iodine.
Heat-Affected Zone	The area adjacent to a weld where a change in microstructure has occurred as a result of the heat during welding, brazing, or cutting, but is not melted during the process.
High Temperature Corrosion	A form of corrosion that refers to corrosion where the electrolyte is a gas rather than a liquid.
Holidays	An undesirable discontinuity that occurs in a coating exposing the base metal to the surrounding environment. Holidays are usually in the form of cracks, gaps, or pores.
Hot Corrosion	A type of high temperature corrosion where the combined effect of oxidation and reactions with sulfur compounds, as well as other contaminants (e.g. chlorides), produce molten salts which deposit onto a surface and consequently degrading or destroy the protective oxide layer.
Hot-Dip Galvanizing (Hot Dipping)	A galvanization process where a base metal is coated by immersing it in a molten zinc bath.
Hull	The body or shell of a watercraft.
Hydrogen Damage	Any deterioration of a material as a result of the presence of hydrogen, whether in the surrounding environment or internal to the material.
Hydrogen Embrittlement	The reduction in load bearing capability and/or decreased ductility of a material as a direct result of reactions with hydrogen.
Hydrogen Induced Cracking	See hydrogen embrittlement.
Hygroscopic	A substance that can absorb moisture from the atmosphere.
Hypochlorite	The negative ion (ClO_3^-) that results when hypochlorous acid (HClO) dissociates; it acts as an oxidizing agent.
Impingement	A type of erosion corrosion usually associated with higher velocity liquid repeatedly interacting with a specific area, such as an elbow in piping units.
Impressed-Current Cathodic Protection	A cathodic protection method that uses an external power source to supply direct current to an electrode; this is to supply the material to be protected with additional electrons to give to a corrosive environment, which would otherwise attack the electrons contained within the material ultimately causing corrosion to occur.
Inhibitor	A chemical substance that reduces corrosion without reaction with the environment.
Integral Fuel Tank	An area within a structure, such as an aircraft wing, that can serve as a container for fuel.
Intergranular Corrosion	A form of corrosion that attacks grain boundaries in materials. It may occur as a result of a galvanic couple between differing phases within a material.

Intergranular SCC	A specific form of SCC where the cracks appear along the grain boundaries.
Interstitial Element	An atom that is positioned at a nonequilibrium site, which is outside or between the regular crystalline lattice structure.
Ion Plating	A coating process in which ions are driven from a plasma by an electrical bias on the substrate where they are deposited. Alternatively, the coating can be applied using an ion beam deposition technique, where plasma ions bombard the substrate to create nucleation sites for a neutral ion species. The neutral species can then deposit onto the nucleation sites, resulting in the formation of a coating
Ion Vapor Deposition	See Ion Plating.
Kinetics	The measure and study of the rates of chemical reactions. It is used to determine the mechanism of reactions.
Lactic Acid	An organic, alpha-hydroxy carboxylic acid ($CH_3CH(OH)COOH$); it is a hygroscopic substance.
Lap Joint	A joint where the two members to be fastened overlap each other.
Laser Alloying	The process of modifying the surface composition of a material using a laser to melt the material's surface and then adding other elements to the melt area, with subsequent solidification.
Laser Peening	A process used to enhance the mechanical properties of a material's surface. This is done by Inducing compressive residual stresses within a material using laser to generate a shockwave near the material's surface.
Laser Shock Processing	See laser peening.
Laser Surface Alloying	See laser alloying.
Life-Cycle Cost	The total costs associated with a system over its service life, and includes the raw materials, fabrication costs, any preventive maintenance and repair costs, and disposal costs (initial, operating, and maintenance costs).
Linear Polarization Resistance	An electrochemical method used to measure instantaneous rates of uniform corrosion and is widely applied for systems in full immersion aqueous environments. A small potential is applied to a sensor electrode with the direct current being measured. The polarization resistance obtained is inversely proportional to the corrosion rate.
Liquid Metal Embrittlement	The brittle failure of an otherwise ductile material when in contact with a liquid metal and subjected to tensile stress.
Liquid Penetrant Inspection	A non-destructive inspection technique used to find surface defects and cracks by applying a penetrating liquid to reveal these damaged areas.
Local Cell	A galvanic cell resulting from potential differences occurring within only a small portion of a material that is in contact with an electrolyte.
Localized Corrosion	Forms of corrosive attack that target specific areas of a material, as opposed to uniform corrosion.
Longitudinal Direction	The direction that is oriented through the width of a 3-D grain.
Long Transverse Direction	The direction that is oriented through the width of a 3-D grain.

Magnetic Particle Inspection	An inspection technique that is used to find surface defects in ferromagnetic materials such as steel and iron. Magnetic particles are dispersed over the material's surface, and a magnetic field is then induced in the material which produces flux lines that are distorted in the presence of defects.
Magneto-Optic Eddy Current Imaging	An inspection method that measures induced eddy currents using a Faraday magneto-optic sensor and displays the measurements on a video monitor.
Martensitic	A stainless steel containing greater than 12% Cr and up to 2.5% Ni. It may be hardened by quenching and tempering.
Microbiological Corrosion	The occurrence of corrosion due to metabolic activity of microorganisms present on a metallic surface.
Microperforation	A type of hydrogen damage, primarily seen in steels, where small fissures are created by high pressure hydrogen at room temperature.
Mineral Acid	A common inorganic acid (e.g. hydrochloric, sulfuric, nitric, etc.).
Molten Salt Corrosion	The occurrence of corrosion in the presence of molten or fused salts; see hot corrosion.
Nitric Acid	A strong mineral acid and strong oxidizer (HNO_3).
Noble	Refers to the resistance to chemical activity or inertness.
Noble Metals	Metals that are highly resistant to chemical activity including oxidation and corrosion (e.g. platinum, gold, etc.).
Open Circuit Potential	The measured cell potential in the absence of an electrical current.
Organic Acid	A chemical compound containing at least one carboxyl group (COOH).
Overaging	Aging process that is taken past the time or temperature requirements for maximizing a certain property in order to achieve other properties.
Oxalic Acid	A strong organic acid also known as ethanedioic acid (($COOH)_2$)
Oxidation Reaction	A chemical reaction that causes a loss of electrons and consequently an increase in valence.
Oxidation-Reduction Reaction	An oxidation reaction that occurs simultaneously with a reduction reaction.
Oxidizing Agent	A compound that provides the means to remove electrons from the reacting species, thus causing an oxidation reaction to occur.
Passivated	The condition when a metal becomes less active (more noble), than its original state in the galvanic series.
Passive	A state of a material that is characterized by its relative inertness to the surrounding environment.
Passive Cathodic Protection	See sacrificial protection.
pH	A logarithmic measure of the concentration and activity of hydrogen ions in solution. The measure of acidity or alkalinity of a solution (e.g. at RT acid solutions have a pH less than 7, while alkaline solutions have a pH greater than 7).

Physical Vapor Deposition	A process where a material is deposited on a substrate via a physical mechanism, that is without changing the chemical composition, and it employs an active gas and plasma to deposit the material uniformly over the entire substrate. Specific PVD methods include ion plating or deposition, sputtering, and laser surface alloying.
Pickling Bath	An acid or alkaline solution that is used to remove oxides from a metal's surface.
Pitting	A form of localized corrosion that occurs when a corrosive medium attacks a metal at specific points and results in deep cavities in the metal.
Plastic Deformation	The permanent change in shape or size of a material without cracking when subjected to a sustained stress or load.
Polarization	The shift in electrode potential during electrolysis.
Potentiostat	A device for controlling the electric potential of an electrode in an electrolyte.
Poultice Corrosion	A specific type of corrosion usually occurring in ground vehicles, where road salt and debris accumulate in hard-to-reach areas, absorb moisture, and consequently cause an acceleration of corrosive attack.
Precipitation Hardening Steel	A process of hardening an alloy by precipitating a constituent from a supersaturated solid solution.
Primer	A first coat of paint designed to have good bonding and wetting characteristics. It may or may not contain inhibitors.
Radiography	A method whereby x-rays, gamma rays, or neutrons are transmitted into a material and the absorption data recorded is then used to find any defects within the material.
Reducing Agent	A compound that provides the means to give up electrons to the reacting species, thus causing a reduction reaction to occur.
Reduction Reaction	A chemical reaction that causes a gain of electrons and consequently a decrease in valence.
Refractory Metals	A group of metals that is heat resistant, and has relatively high melting points.
Residual Stress	Tensile and/or compressive stresses present in a material, free from external forces or temperature gradients. They are typically formed during the fabrication process and remain after the process is finished.
Sacrificial Protection	A method used to reduce the rate of corrosion of a metal by galvanically coupling that metal to a more anodic metal. The anodic metal thus has a greater propensity to corrode, and does so preferentially to protect the less anodic metal from corrosion.
Salinity	A total amount of salt content dissolved in water, as measured in weight.
Scale	The layer of corrosion or oxidation products that initially form on the surface of a metal upon environmental exposure.
Sealant	A coating material, usually applied to a specific area, such as around fasteners or at crevices, to completely encase the area to prevent the penetration of moisture.
Selective Leaching	A localized form of corrosion where a particular element within a material is preferentially attacked and extracted from the material.

Self-Healing Film	A film that has the ability to regenerate itself when the substrate is exposed to a corrosive environment, by reacting with constituents in the environment to reproduce the film.
Sensitization	The formation of precipitates at grain boundaries, by exposure to heat, which provides a mechanism for preferred corrosive attack.
Shatter Cracks	Small cracks in wrought metals due to stresses produced by localized transformation and decreased solubility of hydrogen during cooling from hot working. On a fracture surface, shatter cracks are bright silvery areas while on an etched surface, they appear as short, discontinuous cracks.
Short Transverse Grain Direction	The direction that is oriented through the thickness of a 3-D grain.
Shot Peening	The bombardment of a metal surface by small spherical particles, which induces compressive residual stresses in the metal and effectively increases its fatigue life.
Solid Metal Embrittlement	The embrittlement of a metal when in contact with another metal that is slightly below its melting point.
Solution Heat Treatment	A metal treatment process that uses heating and cooling to cause one or more components of an alloy to enter into a solid solution.
Splash Zone	The zone above the tidal zone and below the atmospheric zone, and is the area where the material or structure is exposed to spray from the waves.
Sputtering	A PVD coating process that uses electrons in an inert gas to bombard a target of coating material and eject particles that are then deposited onto a substrate.
Stray Current Corrosion	Corrosion that is caused by the unintended flow of current through a metal, where the current has originated from an external source.
Stress Corrosion Cracking	A cracking process involving the combined factors of corrosive environment and a sustained tensile stress.
Striation Pattern	A set of parallel ridges that form on the crack face (perpendicular to the crack propagation direction) in a metal exposed to cyclic stresses.
Subcritical Crack Growth	Crack growth in which the crack size is smaller than the crack size resulting in fracture.
Submerged Zone	The zone below the tidal zone, where the material or structure is completely immersed in the water environment.
Sulfate-Oxidizing Bacteria	Type of bacteria known to influence corrosion (microbiological corrosion) by producing sulfuric acid causing a reduction in pH of the environment.
Sulfate-Reducing Bacteria	Type of bacteria known to influence corrosion (microbiological corrosion) by supplying a sulfate ion to cause a reduction reaction with a metal.
Sulfidation	A reaction which inserts a sulfur atom into a compound.
Surface Treatment	A surface treatment is the physical or chemical modification of a material's surface using various means to improve some characteristic of the material, such as corrosion resistance.
Tannic Acid	An organic acid with the chemical formula of $C_{14}H_{10}O_9$.

Thermal Spraying	A type of coating process where particulates are deposited onto the substrate in molten or near-molten form to create a film.
Thermodynamics	The study of the laws and principles that govern the conversion of energy from one form to another, the direction in which heat will flow, and the availability of energy to do work on a system.
Thermography	A technique that measures the infrared radiation a material system emits to detect corrosion, debonding, cracking, thinning, and water absorption, among other defects.
Threshold Velocity	In terms of seawater flowing at a velocity relative to an immersed object, this is the critical velocity at which the dominating mechanism of corrosion changes to erosion corrosion, the rate of which then increases dramatically as a function of velocity.
Throwing Power	The measure of current density at a specific point on a material in relation to the distance from the power source.
Tidal Zone	The zone above the submerged zone and below the splash zone, where the material or structure is exposed to high and low tidal waves.
Tie Coat	A coating layer used to separate two different types of coatings that are incompatible; or a wet sticky coating used to bond two coatings or surfaces that are dry and do not have good adhesion properties.
Transgranular SCC	A form of SCC that occurs across a grain or crystal within a metal.
Ultrasonic Inspection	An inspection technique that uses ultrasonic vibrations to detect flaws or defects in a material.
Uniform Corrosion	A form of corrosion that occurs uniformly over the entire exposed surface of a metal.
Visual Inspection	The inspection of components by observation of light reflected from the surface of an object to the human eye.
Watercraft	Vehicles that are used to navigate on the surface or under the surface of water.
Welding	The process of joining two metals using heat to melt and fuse them together, either with or without a filler metal.
Weldment	A material structure whose components are welded together.
Wicking Material	A material that absorbs water.

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