PDHonline Course G370 (2 PDH)

Galvanizing for Corrosion Protection

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Course Content

Zinc-coated steel is commonly used as a construction material, e.g. for highway guard rails, structural work in bridges and towers, roofing and siding for industrial and farm buildings, ducts in heating and air conditioning systems, pipes and tubing, fencing, and automobile parts. Zinc coated steel is also used for bolts, nuts, screws, nails, hooks, chains and other hardware. In order to understand how galvanizing protects steel from corrosion, it is important to first understand corrosion. Metal corrosion is generally defined as an interaction of the metal with its environment that adversely affects the properties of the metal. Corrosion is an electrochemical process. That is, metal corrosion reactions normally involve both chemical reactions and the flow of electrons. A basic electrochemical reaction that drives the corrosion of metals is galvanic corrosion. In a galvanic cell, current is generated internally by physical and chemical reactions occurring among the components of the cell.

The principal uses of zinc for corrosion control are as a coating for steel and as zinc anodes for cathodic protection. Cathodic protection is an equally important method for preventing corrosion. Cathodic protection requires changing an element of the corrosion circuit, introducing a new corrosion element, and ensuring that the base metal becomes the cathodic element of the circuit.

There are two major variations of the cathodic method of corrosion protection. The first is called the impressed current method. In this method, an external current source is used to impress a cathodic charge on all the iron or steel to be protected. While such systems generally do not use a great deal of electricity, they often are very expensive to install.

The other form of cathodic protection is the sacrificial anode method, in which a metal or alloy that is anodic to the metal to be protected is placed in the circuit and becomes the anode. The protected metal becomes the cathode and does not corrode. The anode corrodes, thereby providing the desired sacrificial protection. In nearly all electrolytes encountered in everyday use, zinc is anodic to iron and steel. Thus, the galvanized coating provides cathodic corrosion protection as well as barrier protection.

Zinc coatings are typically applied by one of four methods. They are;

1. Hot-dip galvanizing,
2. Electrodeposition (i.e. electroplating, is a process for producing a dense, uniform, and adherent coating by the act of passing an electrical current through a bath),
3. Metal spraying (which is often specified in preference to hot dip process for its ease of application without the need for drilling of vent/drain holes and to avoid the risk of distortion), and
4. Sherardizing (a diffusion process in which articles are heated in the presence of zinc dust. The process is normally carried out in a slowly rotating closed container at temperatures ranging from 320-500°C).

Each coating method has certain features and characteristics and these help determine which one should be used for specific purposes. This course will concentrate on the most widely used method, hot-dip galvanizing.

Some of the everyday structures and components that are typically hot-dip galvanized are;

Structural steel for power generating plants, petrochemical facilities, heat exchangers, cooling coils, electrical transmission towers and poles
Bridge structural members, culverts, corrugated steel pipe, and arches
Reinforcing steel for cooling towers, architectural pre-cast concrete, and bridge decks
Pole line hardware and railroad electrification structures
Highway guardrails, signal light and sign poles
Marine pilings and rails
Grates, ladders, and safety cages
Anchor Bolts, Railings, Bearing Plates, Bolts, Cables, Floor Gratings, Manhole Covers, Inspection Catwalks, Pipe Supports, Pipe Fittings, Communication Towers, Recreational Equipment (ski resort lift towers, football stadiums, roller coasters), Antennas, Bicycle Racks, Boat Anchors, Boat Trailers, Buckets, Cable Trays,

Automobile Bodies and Parts, Roll-up Doors, Dock Hardware, Dumpsters, Electrical Enclosures, Fencing, Flagpoles, Garbage Cans, Hardware Items, Park Benches, Picnic Table Frames, Pipe Hangars, Scaffolding, Staircases, Utility Trailers, Wheelbarrows

HOT-DIP GALVANIZING PROCESS

Hot-dip galvanizing is the process of applying a zinc coating to fabricated iron or steel material by immersing the material in a molten bath (at approximately 830°F) consisting primarily of zinc.The process is inherently simple, and this simplicity is a distinct advantage over other corrosion-protection methods.
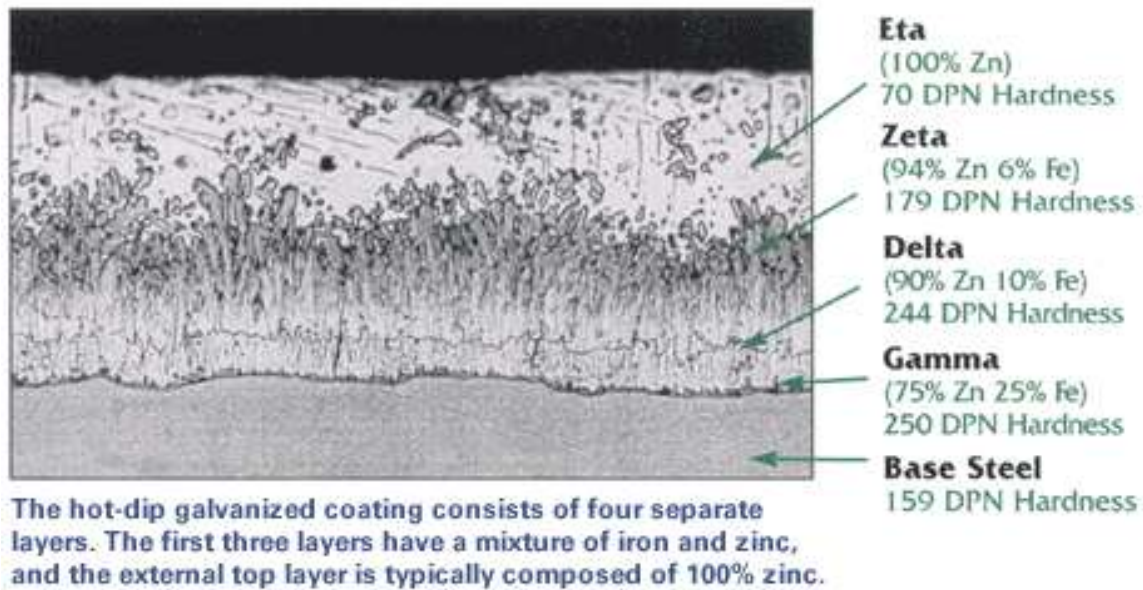

Fabricated items are immersed in the bath long enough to reach bath temperature. The articles are withdrawn slowly from the bath as shown in the above photographs. The excess zinc drains out from the hollow center of poles as they are withdrawn from a molten zinc bath. The poles must have clearance holes at the bottom of the hollow center section to allow for the zinc metal to drain. Tubular fabrications are withdrawn from a molten zinc bath. These parts are vented through small holes near the intersection of tubes to allow the expanding gases to escape and the zinc metal to drain. Small parts and fasteners lie loosely in metal baskets during the galvanizing process. The excess zinc metal is then spun off in a centrifuge to prevent excess zinc from clogging threads.

Coating Structure

Galvanizing forms a metallurgical bond between the zinc and the underlying steel or iron, creating a barrier that is part of the metal itself. During galvanizing, the molten zinc reacts with the surface of the steel or iron article to form a series of zinc/iron alloy layers. The figure below is a photomicrograph of a galvanized steel coating cross-section and shows a typical coating microstructure consisting of three alloy layers and a layer of pure metallic zinc.

Progressing from the underlying steel surface outward, these are: The thin Gamma layer composed of an alloy that is 75% zinc and 25% iron, the Delta layer composed of an alloy that is 90% zinc and 10% iron, the Zeta layer composed of an alloy that is 94% zinc and 6% iron, and the outer Eta layer that is composed of pure zinc. The figure below also indicate the respective hardness of each layer expressed in Diamond Pyramid Number (DPN), also known as Vickers hardness.

Eta
(100% Zn)
70 DPN Hardness

Zeta
(94% Zn 6% Fe)
179 DPN Hardness

Delta
(90% Zn 10% Fe)
244 DPN Hardness

Gamma
(75% Zn 25% Fe)
250 DPN Hardness

Base Steel
159 DPN Hardness

The hot-dip galvanized coating consists of four separate layers. The first three layers have a mixture of iron and zinc, and the external top layer is typically composed of 100% zinc.

The intrinsic corrosion resistance of zinc lies in its ability to form dense and adherent corrosion-product films which resist further metallic corrosion. Initially, a fresh zinc surface corrodes fairly rapidly until it is covered with protective corrosion product films. The process then continues at a reduced rate. Often, the rate is linear, in other words, stays constant over time. Under some conditions, such as highly polluted industrial atmospheres, the corrosion rate may increase with continued exposure. In some cases, such as marine atmospheres, the rate has been found to decrease with time.

In addition to zinc's tendency for the formation of protective film, the low corrosion rate of zinc results from the high hydrogen overvoltage of a zinc surface in aqueous solutions. This limits the rate at which hydrogen reduction, and hence corrosion, occur on zinc. In deareated water or in nonoxidizing solutions, hydrogen overvoltage can be a major factor in controlling the corrosion rate.

The combined factors of corrosion-product build-up and high hydrogen overvoltage give zinc an atmospheric corrosion rate that is often as low as one twenty-fifth that of steel. The exact ratio of zinc and steel corrosion rate depends on the speciific exposure environment.

As long as a zinc coating is continuous and uniform, it will corrode like solid zinc. If, however, the base metal becomes exposed through some break or corroded zone in the zinc coating or during fabrication (i.e. sheared edges of galvanized coil), the galvanic protection properties of zinc will come into effect. Steel being more electro-negative than zinc, it will attract electrons from zinc. This flow of electrons will reduce the corrosion rate of steel while increasing that of the zinc. The zinc coating is thus sacrificed to prevent the steel at the exposed areas.

Bond Strength

As mentioned earlier, along with the name of each layer in the figure above (magnified cross-section of hot-dip galvanized coating) appears its respective hardness, expressed by a Diamond Pyramid Number (DPN). The DPN is a progressive measure of hardness; the higher the number, the greater the hardness. Typically, the Gamma, Delta and Zeta layers are harder than the underlying steel. The hardness of these inner layers provides exceptional protection against coating damage by abrasion. The Eta layer is quite ductile, providing the coating with some impact resistance. The galvanized coating is adherent to the underlying steel on the order of several thousand pounds per square inch (psi). Other coatings typically offer adhesion rated at several hundred psi at best. Hardness, ductility and adherence combine to provide the galvanized coating with unmatched protection against damage caused by rough handling during transportation to and/or at the job site, as well as in service. The toughness of the galvanized coating is extremely important since barrier protection is dependent upon the integrity of the coating.

Coating Uniformity

The galvanizing process naturally produces coatings that are at least as thick at the corners and edges as the coating on the rest of the article. As coating damage is most likely to occur at the edges, this is where added protection is needed most. Brush-or spray-applied coatings have a natural tendency to thin at the corners and edges. The figure below is a photomicrograph showing a cross-section of a corner of a galvanized piece of steel where the coating is uniform.
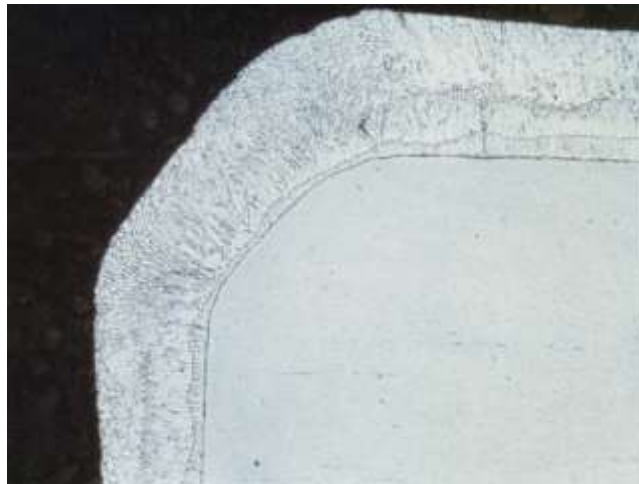
Because the galvanizing process involves total immersion of the material, all surfaces are coated. Galvanizing provides protection on both exterior and interior surfaces of hollow structures. Hollow structures that are painted (but not galvanized) have no corrosion protection on the inside.

The inspection process for galvanized items is simple and fast and requires minimal labor. This is important because the inspection process required to assure the quality of many brush- and spray-applied coatings is highly labor-intensive and uses expensive skilled labor. Furthermore, galvanizing takes place in a factory regardless of weather or humidity conditions. Most brush- and spray-applied coatings depend upon proper weather and humidity conditions for correct application. This dependence on atmospheric conditions often translates into costly construction delays. The galvanizer's ability to work in any type of weather allows a higher degree of assurance of on-time delivery. Working under these circumstances, galvanizing can be completed quickly and with short lead times.

Coating Designations

There are several types of products that are fabricated from carbon steel sheet that has been coated with zinc on two sides by the continuous hot-dip process. The process results in a layer of zinc on each side of the steel sheet that is tightly adhered to the steel sheet through the formation of an iron-zinc alloy bonding layer that is formed by a diffusion process while the heated steel strip is in contact with the molten zinc. The relatively pure zinc coating exhibits a bright metallic color with a pronounced "spangled" appearance. These coatings have a free zinc spangled surface and may be processed in a manner that reduces spangle and results in a smooth dull-gray appearance. This type of coating is referenced with a "G" designation (or "Z" in SI Units).

Each coated-steel sheet product has a coating weight designation system that is in common use today. The system for each type of coating is defined in the appropriate ASTM standard. For example, the most commonly used ASTM standard is A 653/A 653M which covers hot-dip galvanized products. The coating weight designation system is given in terms such as G60, G90, etc. These numbers refer to the weight (mass in SI units) of zinc on the surface of the steel sheet in Inch-Pound (English or Imperial) units of measurement. That is, for G90, the coating on one square foot of sheet (total coating, both sides of the sheet) weighs a minimum of 0.90 ounces. If equally applied to both sides of the sheet, there would be a minimum of 0.45 ounces on each surface.

The other measurement system in widespread use today is the SI (Metric) system. The conversion from the Inch-Pound weight in ounces per square foot (oz/ft^2) to the SI mass in grams per square meter (g/m^2) is:

$$1 \ oz/ft^2 = 305.15 \ g/m^2$$

To convert from oz/ft^2 to g/m^2, multiply by 305.15

Example: G90 (0.90 oz/ft^2) = Z275 (275 g/m^2)

Since what we are most interested in is the coating thickness, why don't the ASTM standards use thickness measurements? The answer is simply that it is difficult to directly measure the thickness accurately. For example, a G90 coating contributes about 1.6 mils (0.0016 inches) of thickness to the final coated sheet. For a coating equally applied to both sides of the sheet, this means there is about 0.0008 inches of zinc on each surface. Thus, to accurately determine the thickness of the coating, one needs to know the precise thickness of the steel and then use a thickness gauge capable of accurately reading to the nearest ten thousandth of an inch. It is much easier, and more accurate, to use a "weigh-strip-weigh" procedure to determine the weight of coating. Weigh-strip-weigh refers to the technique of weighing a standard-sized sample of the product using a very accurate scale, then stripping the coating in a mild acid to remove only the coating, then reweighing the coupon to determine the weight loss. Hence, the origin of the term "weigh-strip-weigh". There are weigh-strip-weigh procedures that can be used for all zinc-based coatings in commercial production today. For the most common products, these procedures are defined in ASTM Standard A 90/A 90M, and cover galvanized and galvannealed coated sheet, Galvalume coated sheet, and Galfan coated sheet. There are special procedures required for other types of alloy coatings such as zinc-nickel alloy electroplated sheet. These are covered by other ASTM standards.

Galvannealed products are fabricated from carbon steel sheet that has been coated by the continuous hot-dip process and further treated to convert the zinc coating into a zinc-iron alloy. The zinc coated sheet receives an in-line heat treatment immediately as the strip exits the molten zinc bath to convert the entire coating layer to a zinc-iron alloy by diffusion of iron from the sheet into the zinc coating. The galvannealed surface has a non-spangled matte finish with a nominal composition of 90% zinc and 10% iron. This type of coating is referred to with an "A" designation (or "ZF" in SI Units).

Although the corrosion resistance is slightly lower, the galvannealed coating has several advantages compared to the galvanized coating: 1) improved paint adhesion; 2) the coated surface accepts paint very readily without a pretreatment (a pretreatment will enhance the performance); 3) the zinc-iron alloy coating can be welded more easily; and 4) the coating is harder and more resistant to manufacturing processes.

The average coating thickness specified in table below is based on the conversion factor of one ounce of zinc coating per square foot of surface corresponding to an average coating thickness of 0.0017" (0.043 mm). This coating thickness is not significant enough to make an appreciable difference in the measurable thickness of coated or uncoated steel of the same gage. Table below shows a sampling of coating designations, minimum coating weights, and corresponding average coating thicknesses.

Corrosion resistance is directly proportional to coating weight. The heavier the coating weight the more zinc is present and the more corrosion protection it will provide. Therefore, under similar atmospheric conditions a 60 designation will provide 50% more corrosion protection than a 40 designation coating.

Table: Coating designations, minimum coating weights, and average coating thickness

Type	Coating Designation		Coating Weight				Average Coating Thickness / Side	
			Minimum Check Limit Triple Spot Test		Minimum Check Limit Single Spot Test			
	In-lb	SI	oz/ft^2 *	g/m^2 *	oz/ft^2 *	g/m^2 *	inch	mm
Galvanized	G60	Z180	0.60	180	0.50	150	.0005	.013
	G40	Z120	0.40	120	0.30	90	.0003	.009
Galvannealed	A60	ZF180	0.60	180	0.50	150	.0005	.013
	A40	ZF120	0.40	120	0.30	90	.0003	.009

* NOTE: The weight of coating refers to the total coating on both surfaces.

## FACTORS EFFECTING COATING THICKNESS

The American Society of Testing and Materials International (ASTM), the Canadian Specification Association (CSA) and the American Association of State Highway and Transportation Officials (AASHTO) specifications establish minimum standards for thickness of galvanized coatings on various categories of items. These minimum standards are routinely exceeded by galvanizers due to the nature of the galvanizing process.

Factors influencing the thickness and appearance of the galvanized coating include chemical composition of the steel, steel surface condition, cold-working of steel prior to galvanizing, bath temperature, bath immersion time, bath withdrawal rate, and steel cooling rate.

Base Steel and Coating Composition

The chemistry of the steel being galvanized influences the galvanized coating's appearance. Depending on the chemistry of the steel, the appearance will range from a normal bright shiny coating to a dull grey coating. While a gray or matte appearance may occur, the corrosion protection afforded is no different than that provided by shinier galvanized coatings. The corrosion resistance of matte coatings, mil for mil, is equal to the more typical bright, shiny galvanized coating.

**Effects of Killed and Unkilled Steel on Coating Weight**
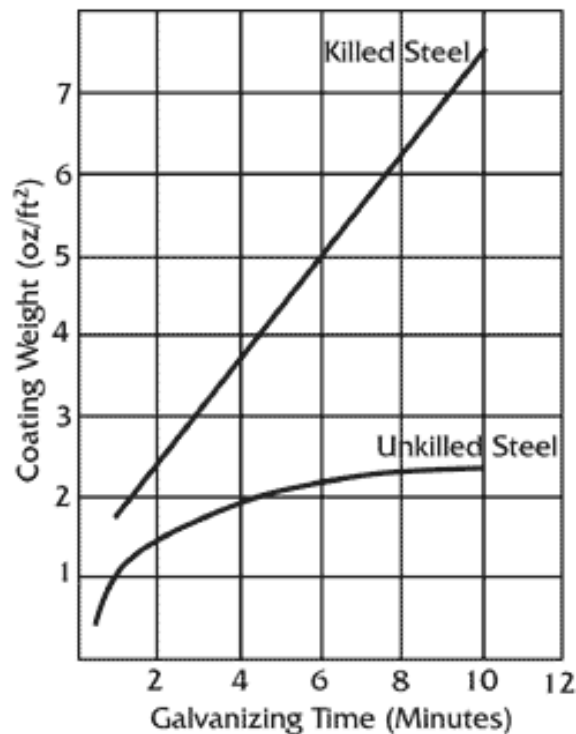
The amount of silicon and phosphorus in the steel strongly influences the thickness and appearance of the galvanized coating. Silicon, phosphorous or combinations of the two elements can cause thick, brittle galvanized coatings. Brittle coating may crack or flake off during forming and bending operations. The coating thickness curve shown in the figure below relates the effect of silicon in the base steel to the thickness of the zinc coating. The carbon, sulfur and manganese content of the steel also may have a minor effect on the galvanized coating thickness.

Hot-dip coatings seldom consist of high purity zinc. Often lead is added to the plating bath to produce a smoother finish while aluminum is included to reduce the thickness of the iron-zinc diffusion zone.
The effects of these and other elements on the corrosion resistance of the coating are listed below:

- Small additions of aluminum decrease the corrosion resistance of zinc, especially if lead is also present. Aluminum appears to increase intergranular attack in zinc.
- Copper improves atmospheric corrosion resistance.
- Magnesium improves the corrosion resistance of zinc somewhat, especially by counteracting the bad effects of aluminum.
- Small amounts of chromium, nickel, or titanium can be beneficial for zinc's corrosion resistance.
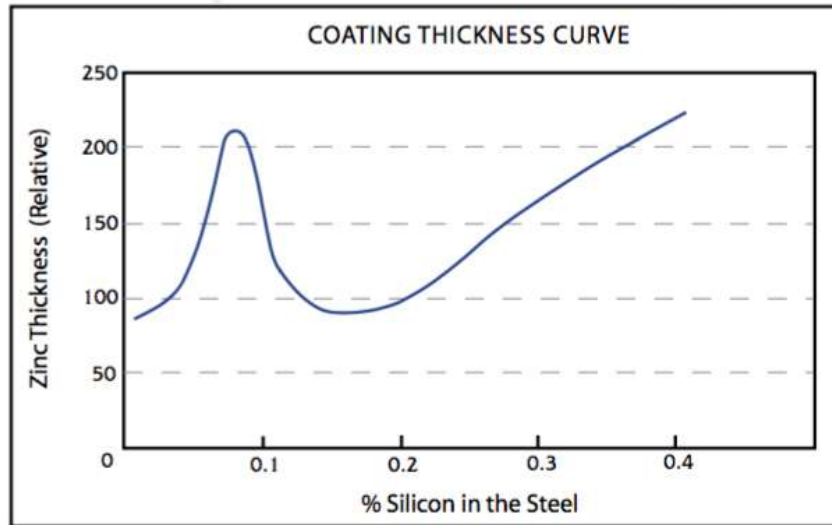
Effect of silicon content on coating thickness

The combination of elements mentioned above, known as "reactive steel" in the galvanizing industry, tends to accelerate the growth of zinc-iron alloy layers. This may result in a finished galvanized coating consisting entirely of zinc-iron alloy. Instead of a shiny appearance, the galvanized coating will have a dark gray, matte finish. This dark gray, matte coating will provide as much corrosion protection as a galvanized coating having a bright appearance.It is difficult to provide precise guidance in the area of steel selection without qualifying all of the grades of steel commercially available. The guidelines discussed below usually result in the selection of steels that provide good galvanized coatings.

Levels of carbon less than 0.25%, phosphorus less than 0.04%, or manganese less than 1.35% are beneficial. Silicon levels less than 0.04 % or between 0.15% and 0.25% are desirable.

Even though it is not a part of the controlled composition of the steel, silicon may be present in many steels commonly galvanized. This occurs primarily because silicon is used in the deoxidization process in steel making and is found in continuously cast steel (silicon-killed steel). The phosphorus content should never be greater than 0.04% for steel that is intended for galvanizing. Phosphorus acts as a catalyst during galvanizing, resulting in rapid growth of the zinc-iron alloy layers. This growth is virtually uncontrollable during the galvanizing process.

The galvanizing characteristics of various steels are given below:

1. High silicon steels will produce thick galvanized coatings that may be brittle because the steel reacts very rapidly with the zinc. The effects of high silicon content can be minimized by keeping the immersion time in the zinc bath as short as possible. This becomes increasingly difficult as section thickness increases.
2. High manganese steels will produce brownish colored coatings that may be brittle and easily damaged in handling compared to galvanized coatings on conventional steels.
3. High carbon steels can be successfully galvanized as long as their yield strength is within an acceptable range (see note 9 below).
4. High sulfur steels are used for high-speed machined components (threaded fasteners, sockets etc.) and should not be galvanized. The high sulfur steel can be severely eroded in the galvanizing process, rendering threaded items unserviceable.
5. High phosphorus steels are rarely encountered in galvanizing operations but are unsuitable for galvanizing. They react rapidly with the zinc to form thick, dark coatings that are easily damaged and may delaminate from the surface.
6. Stainless steels can be galvanized but are susceptible to liquid metal embrittlement and can fracture under load after immersion in molten zinc. Stainless steels are only galvanized incidentally if they are

attached to mild steel assemblies.

7. Cast iron and steel will normally galvanize satisfactorily, but molding sand fused to the surface will not be removed by the pre-treatment process. Cast items may require abrasive blasting prior to delivery to the galvanizing plant to remove these refractory surface contaminants.

8. Very low alloy steel has a very low reaction rate with zinc, and can cause problems in producing galvanized coatings that comply with standards. It is most frequently found in products that are formed from low-strength (under 350 MPa) steel coil.

9. High strength steels (over 800 MPa [115,000 psi] yield strength) are susceptible to hydrogen embrittlement arising from the pickling process in galvanizing. Pickling should be avoided for steels in this strength range.

As the galvanizing reaction is a diffusion process, higher zinc bath temperatures and longer immersion times generally will produce somewhat heavier alloy layers. Like all diffusion processes, the reaction proceeds rapidly at first and then slows as layers grow and become thicker. However, continued immersion beyond a certain time will have little effect on further coating growth. When galvanizing reactive steels, the diffusion process proceeds at a faster rate, producing thicker coatings.

The thickness of the outer pure zinc layer is largely dependent upon the rate of withdrawal from the zinc bath. A rapid rate of withdrawal causes an article to carry out more zinc and generally results in a thicker coating. ASTM, CSA and AASHTO specifications and inspection standards for galvanizing recognize that variations occur in both coating thickness and compositions. Thickness specifications are stated in average terms. Further, coating thickness measurements must be taken at several points on each inspected article to comply with structural steel and hardware specifications.

Coating Appearance

For years, galvanized articles made by hot-dip coating techniques were identified by the characteristic spangled appearance. In many cases, this is still true today. However, because of some changes in the manufacturing processes associated with zinc production and the galvanizing process, not all hot-dip galvanized steel sheet made today has a visible spangle. The dictionary defines "spangle" as a glittering object. When spangle is used to define the surface appearance of galvanized steel sheet, it includes the typical snowflake-like or six-fold star pattern that is visible to the unaided eye, which is the dendritic solidification pattern of the coating. The crystalline structure can range from large, very visible dendritic grains to small, equiaxed grains that are difficult to discern with the unaided eye. Variables that affect the crystal size and visibility include: steel substrate composition and prior treatment, coating bath composition, coating solidification rate and post coating processing such as temper rolling. The following photograph shows the details of the typical spangle pattern of a galvanized coating. The surface is magnified about 20X.

The Solidification Process

First, one needs to understand that the development of spangles occurs when the molten zinc adhering to the steel sheet is cooled below the melting point of zinc. The freezing point is approximately 419°C (787°F). At this temperature, the randomly arranged atoms in the liquid zinc begin to position themselves into a very orderly arrangement. This occurs at many random locations within the molten zinc layer. This transformation from a disordered arrangement of the atoms into an orderly arrangement defines the "solidification" or "crystallization" process. The small solidifying areas within the molten zinc are defined as "grains". As the individual atoms of molten zinc attach themselves to a solidifying grain (causing grain growth), they form into a distinct array, or crystal. In the case of zinc, the crystals form with hexagonal (six-fold) symmetry. It is this fundamental way in which the individual atoms of zinc arrange themselves as the solid zinc grains grow larger that leads to the often-visible hexagonal symmetry of the final spangle. When the coating is finally completely solidified, the individual spangles define specific individual grains of zinc.

Historically, users relied on the spangled appearance to distinguish hot dip galvanized from less corrosion resistant thin electroplated steel (a typical example is illustrated below where the grains are clearly evident on a light pole). In order to maintain this distinction, it became common practice to add lead (typically about 0.1%) to keep the spangles, even after refining methods for producing lead-free zinc were developed. With increasing environmental concerns, however, the use of lead has declined. Antimony has replaced lead as the spangle-promoting agent. Spangles are also prone to cracking, a phenomenon in which cracking occurs along certain crystallographic planes during forming of the coated sheet. For painted end uses, such as automobiles and metal buildings, a smoother, nonspangled surface is desirable for appearance purposes.

"Nucleation" is the term used to define the process of transformation of randomly arranged atoms of molten metal into a small, organized array of atoms in the "seed" crystals at the initial stage of solidification. A high rate of nucleation during the freezing process would tend to cause the formation of numerous small grains in the final solidified structure, while a low rate of nucleation would tend to favor the growth of large grains, as shown in the below photograph of a highway barrier with extremely large grains.

There is another aspect of the solidification process that leads to the snowflake pattern in galvanized coatings, "dendritic" (meaning tree-shaped) growth. Dendritic growth causes the individual growing (solidifying) grains to grow into the melt (the molten zinc coating) with a distinct leading rounded edge. A "primary" dendrite arm is identified in the photograph above. There are secondary dendrite arms that grow laterally away from the "primary" dendrite arms.

Dendritic growth of grains during the solidifying of metals is very common. The reason that the dendrites are readily visible in a galvanized coating is that we are basically seeing a two-dimensional version of an as-cast, dendritic, solidified grain structure. Remember, the coating is typically around 0.001 in (25 µm) thick, considerably less than the diameter of a spangle. In other metals (for instance in the steel substrate), the original as-cast, three- dimensional, dendritic structure of the grains is subsequently broken up into many smaller, more equiaxed grains. This is related to the effects of hot rolling (for example, rolling a 9-inch thick slab of steel into a 0.050-inch thick steel sheet), cold rolling and recrystallization during the sheet-annealing process.

The rate of growth of the dendrite arms during the solidification of a galvanized coating competes with the rate of nucleation of new grains within the molten zinc. This process determines the final size of the completely solidified structure. In the case of the above photograph, which is a galvanized coating with a well-defined large spangle pattern, the rate of dendrite growth dominated the solidification process leading to a small number of large spangles. One characteristic of such spangles is that they are thickest at their centers and thinnest at their edges, or grain boundaries. The grain boundaries can be said to be "depressed" and are difficult to smooth by subsequent temper passing.

Dendritic growth is not the only way in which grains can grow during the solidification process. It requires one or more special conditions to be present. One of these conditions is the presence of other elements in the molten metal. These can be either intentionally added alloying elements or impurities. In the case of galvanized coatings on steel sheet, the most common reason for the well-defined dendritic growth pattern is the presence of lead in the coating. It has long been thought that the reason lead results in large spangles is that it has the effect of reducing the number of nucleation sites. In recent work, it is proposed that that the presence of lead decreases the solid/liquid interfacial energy in the solidifying coating. This leads to an increase in dendrite growth velocity, resulting in large spangles. Lead precipitates at the coating surface and the varying distribution of lead particles across the surface define the optical appearance (dull vs. shiny spangles). Lead is a common impurity in zinc. In years gone by, the most common form of zinc metal production involved smelting, distillation and condensation. Lead is a common metal found in zinc-containing ores, and this refining process carried it through as an impurity in the zinc. Therefore, in the early days of galvanizing, lead was almost always present in the zinc, and it was common to see the spangle pattern. Galvanized coatings on steel became identified by the characteristic spangle. Essentially, all hot-dip galvanized coatings had a spangled appearance. If the spangle wasn't visible, the users "knew" that the steel had not been galvanized.

The first galvanized coatings contained as much as 1% lead. During the past 25 years, the presence of such high lead levels has not been common in the galvanized coatings on steel sheet, at least not in North America, Europe, and Japan. Typical concentrations of lead in most galvanized sheet made during the past 25 years are less than 0.15%, often as low as 0.03 to 0.05%. However, this amount of lead is still sufficient to develop dendritic growth behavior during the solidification process. Today, a typical level of lead in the coating bath on lines where the primary product has a well-developed spangle pattern is in the range of 0.05 to 0.15% lead.

In recent times, the production of zinc from zinc-containing ores has been changed to an electrolytic recovery method. In this method of zinc production, the refined zinc is very pure, with the lead being excluded. This change occurred at a time when many users of galvanized sheet, especially those desiring a high quality finish after painting, such as the automotive and appliance industries, needed a non-spangled coating. Removing the lead gave them the product they desired. The amount of lead in the coating for lead-free coatings is less than 0.01%.Lead-free coatings still have a grain pattern that is visible to the unaided eye. Typically, the spangles are about 0.5 mm in diameter and are clearly visible when seen at 5 to 10X magnification. However, the grains no longer grow by a dendritic mode but by a cellular mode of growth.

Essentially, the grains of zinc nucleate on the steel surface, and grow outward toward the free surface. The absence of lead takes away the strong driving force for growth in the plane of the sheet, preventing the formation of large spangles. Rapid spangle growth cannot occur and the absence of lead results in the coating appearing uniformly shiny. This non-spangled coating, when combined with temper rolling by the galvanized-sheet producer, can be made very smooth. The large grain boundary depressions and surface relief of a spangled coating are not present. The coating can be painted to give a very smooth, reflective finish. An added advantage of producing a lead-free galvanized coating is that is not susceptible to a problem known as intergranular corrosion. This is a coating failure mechanism in damp environments caused by the lead concentrating at the spangle boundaries.

The manufacture of non-spangled coatings, or lead-free coatings, is not easily done. The reason relates to the influence of even a small amount of impurities, such as lead, on the viscosity of the molten zinc. It is difficult to avoid small sags and ripples in the coating when the lead is totally removed. The thicker the coating, the greater the tendency to form sags and ripples. Fortunately, the automotive and appliance industries need only relatively thin coatings (typically 60 to 80 g/m^2/side) of zinc to obtain the level of corrosion resistance their customers demand. Also, the products used by these industries are made on relatively new high-speed lines, or older lines that have been refurbished to allow production at high speeds. The combination of high processing speeds andlow coating weights allows the producer to use lead-free coating baths, avoid the development of spangles, and still attain a smooth coating.

If the end user requires a heavier coating mass (100 g/m^2/side and higher), there is a distinct tendency for the coating, when applied from a lead-free bath, to develop very visible sags and ripples. The result is that the surface is not smooth and the coating locally is composed of thick and thin regions. This tendency for sags is exacerbated a low line speeds (<75 meters/minute). Thus, older, low speed coating lines, lines designed to process heavy-gauge sheet, and those that are used to make heavy coating weight products (275 g/m^2 meter or G90 and heavier) typically still have some amount of lead in the coating bath to improve the final coating uniformity.

The net result is that the final product from many lines still has a visible spangle pattern. This meets with the marketplace needs in that a number of industries, especially those that use bare (unpainted) galvanized sheet, still want the large, bright, reflective spangle pattern. Some galvanized-sheet manufacturers have established practices on their older or low-speed lines where they use essentially lead-free zinc, but add a small amount of antimony to the zinc coating bath. The antimony addition accomplishes the same influence on viscosity and spangle formation as lead. The final result is a smooth, visible spangle coating. Typically, the amount of antimony in the coating bath is about 0.03 to 0.10%.

Surface Preparation

Surface preparation is the most important step in the application of any coating. In most instances where a coating fails before the end of its expected service life, it is due to incorrect or inadequate surface preparation.Surface preparation is essential in order to ensure a top-quality galvanized coating. Steel must be entirely clean for the metallurgical reaction between it and molten zinc to occur and the galvanized coating to form.Common residues found on steel, rough surfaces, heat-treating-induced surface oxides, rust, and other surface contaminants need to be removed prior to galvanizing, as they may prevent the formation of a consistent and uniform zinc coating.

It is important to understand that:

- Rough steel surfaces resulting from fabrication methods or abrasive cleaning processes may   cause thicker zinc coatings
- Cast surfaces must often be abrasively cleaned to remove sand that will prevent zinc adhesion
- Heat-treating often introduces a surface oxide layer that must be removed either by conventional chemical cleaning processes or by blast-cleaning
- Steel surfaces that have varying degrees of rusting require varying amounts of time in the cleaning stages of the galvanizing process, resulting in a variety of surface finishes

- Welding slag that adheres to the steel surface must be removed prior to galvanizing
- The use of cutting oil should be minimized when planning to galvanize; if cutting oil use is unavoidable, the galvanizer should be consulted to determine if normal chemical cleaning processes will remove it from the surface or if another means of removal is necessary.

The surface preparation step in the galvanizing process has its own built-in means of quality control in that zinc simply will not react with a steel surface that is not perfectly clean. Any failures or inadequacies in surface preparation will be immediately apparent when the steel is withdrawn from the molten zinc because the unclean areas will remain uncoated.

Surface preparation for galvanizing typically consists of three steps:(1) degreasing/caustic cleaning; (2) acid pickling; and (3) fluxing.

Degreasing/Caustic Cleaning: A hot alkali solution often is used to remove organic contaminants such as dirt, paint markings, grease, and oil from the metal surface. Epoxies, vinyl coatings, asphalt, or welding slag must be removed before galvanizing by grit/sand-blasting, or other mechanical means. An acidic degreasing agent at ambient or slightly above ambient temperatures can be used as an alternative for removing light oil. Other biodegreasers exist that perform the same cleaning action as caustic solutions.

Pickling: Scale and rust normally are removed from the steel surface by pickling in a dilute solution of hot sulfuric acid or ambient temperature hydrochloric acid. Surface preparation also can be accomplished using abrasive cleaning as an alternative to or in conjunction with chemical cleaning. Abrasive cleaning is a process whereby sand, metallic shot or grit is propelled against the steel material by air blasts or rapidly rotating wheels.

Fluxing is the final surface preparation step in the galvanizing process. Fluxing removes oxides and prevents further oxides from forming on the surface of the metal prior to galvanizing and promotes bonding of the zinc to the steel or iron surface. The method for applying the flux depends upon whether the particular galvanizing plant uses the wet or dry galvanizing process.

In the dry galvanizing process, the steel or iron materials are dipped or pre-fluxed in an aqueous solution of zinc ammonium chloride. The material is then thoroughly dried prior to immersion in molten zinc. In the wet galvanizing process, a blanket of liquid zinc ammonium chloride is floated on top of the molten zinc. The iron or steel being galvanized passes through the flux on its way into the molten zinc.

Galvanizing

In this step, steel is completely immersed in a bath consisting of a minimum 98% pure molten zinc. The bath chemistry is specified by the American Society for Testing and Materials (ASTM) in Specification B6. The bath temperature is maintained at about 830°F (443°C). Fabricated items are immersed in the bath long enough to reach bath temperature. The articles are withdrawn slowly from the galvanizing bath and the excess zinc is removed by draining, vibrating and/or centrifuging.

The chemical reactions that result in the formation and structure of the galvanized coating continue after the articles are withdrawn from the bath, as long as these articles are near the bath temperature. The articles are cooled in either water or ambient air immediately after withdrawal from the bath.

There are two different types of galvanizing kettles: dry and wet. In the dry galvanizing process, the steel or iron materials are dipped or pre-fluxed in an aqueous solution of zinc ammonium chloride. The material is then thoroughly dried prior to immersion in molten zinc. In the wet galvanizing process, a blanket of liquid zinc ammonium chloride is floated on top of the molten zinc. The iron or steel being galvanized passes through the flux on its way into the molten zinc. The flux blanket is then pushed aside to allow for clean removal of the material from the zinc.

FACTORS TO CONSIDER/PROBLEMS TO AVOID

Embrittlement

Embrittlement of steel as a result of the hot dip galvanizing process is rarely encountered with structural grades of steel. However, the use of higher-strength steel grades or inappropriate fabrication techniques can lead to embrittlement problems with galvanized steel.

There are three types of embrittlement encountered in the hot dip galvanizing process. These are:

1. Hydrogen embrittlement,
2. Strain-age embrittlement and,
3. Liquid metal embrittlement.

Hydrogen embrittlement does not result from the hot dip galvanizing of ordinary unalloyed and low-carbon mild steels. Any hydrogen absorbed during pickling is effectively eliminated on immersion in the zinc bath because of the relatively high temperature. It is most commonly encountered and affects steels with yield strengths above 800 MPa. Hydrogen atoms from the acid pickling process penetrate the material and migrate to grain boundaries of these high strength steels leading to brittle fractures under certain conditions. Many high strength steels can be galvanized and standard pre- or post-galvanizing treatmentsare available to eliminate the risk of hydrogen embrittlement. Heating to 300°F after pickling and before galvanizing in most cases results in expulsion of hydrogen absorbed during pickling (typically referred to as baking treatment). Abrasive blast cleaning followed by flash pickling may also be employed when over-pickling is of concern or when high strength steels must be galvanized. The abrasive blast cleaning does not generate hydrogen while it is cleaning the surface of the steel. The flash pickling after abrasive blast cleaning is used to remove any final traces of blast media before hot-dip galvanizing.

Strain-age embrittlement is caused by excessive cold working of the steel prior to galvanizing. The heat of the galvanizing process accelerates the embrittlement, so susceptible steels present a long-term embrittlement risk, even if they were not galvanized. Localized heating of severely cold worked steels through welding may also precipitate stain-aging failure. Bending steel through too tight a radius, re-bending already cold worked steel, or hole punching through thick sections are all manufacturing processes that can give rise to strain-age embrittlement problems. The extent of embrittlement depends on the amount of strain, time at aging temperature, and steel composition, particularly nitrogen content. Elements that are known to tie up nitrogen in the form of nitrides are useful in limiting the effects of strain aging. These elements include aluminum, vanadium, titanium, niobium, and boron. Many manufacturing standards for products such as re-bar address this issue within the standard, and fabricators and manufacturers who abide by established practices and use appropriate steel grades rarely experience problems.

Liquid metal embrittlement is specific to certain types of steels that are infrequently encountered in the galvanizing process. The most susceptible are many grades of stainless steel that from time to time, are attached to mild steel assemblies as fittings or components.The molten zinc penetrates the grain boundaries of these steels and fracture under load may result. If the use of stainless steel components is required, mechanical attachments after galvanizing is strongly recommended.

Sweep and Camber

Protection against corrosion begins at the drawing board. No matter what corrosion protection system is used, it must be factored into the product's design. When the decision is made to hot-dip galvanize, the design engineer must ensure that the pieces can be fabricated for highest-quality galvanizing.

The temperature cycle of the hot-dip galvanizing process can alter the shape of non-symmetrical steel products. In light gauge materials this process can be corrected by strengthening the pieces after galvanizing.

Asymmetrical designs or structures containing sections of unequal thickness can be successfully galvanized, as can fabrications where cold-working techniques (bending, hole-punching, rolling, shearing) are employed. However, certain precautions must be taken.

Steel being galvanized progresses through a temperature cycle upon immersion into and withdrawal from the galvanizing bath. Because parts are immersed at an angle, uneven heating occurs, creating a temperature profile along the part being galvanized. This temperature profile allows the steel's internal stresses to be relieved at different times in the immersion cycle. These stresses may cause changes in shape and/or alignment.

When a larger structural piece is distorted by the hot-dip galvanizing thermal cycle, the piece can be rendered unusable and result in a significant cost to the job. Following the design practices in ASTM A384 will minimize warpage and distortion

The following steps can be taken to minimize the risk of distortion or embrittlement:

- Use assembly parts that are of equal or near-equal thickness, especially at joint
- Use standard rolled shapes
- Use symmetrically rolled sections rather than angle or channel frames; I-beams also are preferred to angles or channels
- Galvanize a channel frame with a plate separately and bolt or weld post-galvanizing

- Bend members to the largest acceptable radii to minimize local stress concentration (ASTM A 143)
- Accurately pre-form members of an assembly so that it is not necessary to force, spring, or bend them into position during joining
- Avoid designs that, because of size, require more than one dip into the molten zinc bath (progressive galvanizing)
- Relieve welding- or cold-working-induced stresses by heat-treating the part at 1100°F (590°C) for one hour per inch (2.5 cm) of section thickness (Large members may be able to be relieved of stresses through vibratory stress relieving process)
- Consult your galvanizer regarding the use of temporary bracing or reinforcing
- The guidelines for safeguarding against warping and distortion during hot-dip galvanizing of steel assemblies are outlined in ASTM A 384.
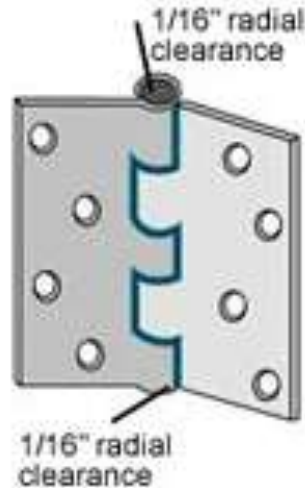
Moving Parts

It is possible to galvanize moving parts. However, during the galvanizing process, steel is immersed into a kettle of molten zinc that forms a corrosion resistant metallurgical bond between steel and zinc. Upon removal from the kettle, the once-molten zinc metal will solidify. As a result, the possibility exists for moving parts, such as drop-handles, shackles, shafts and hinges, to freeze together.
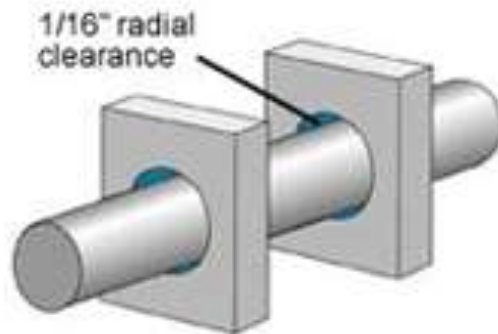
A moving part is difficult to hot-dip galvanize since the zinc metal wants to fill up the gap between two adjacent metal surfaces. Moving parts are best galvanized separately and then assembled.

Best practice indicates that galvanizing prior to assembly will ensure that the full range of motion for moving parts is maintained. If moving parts must be galvanized after assembly, increased radial clearance should be incorporated into the design.

With the proper clearance design, a moving part assembly, such as a door hinge, can be galvanized successfully.

All hinges to be galvanized should be of the loose-pin type.

Hole Sizes

Hot-dip galvanizing applies a coating of zinc on bare steel; therefore, the original steel becomes slightly thicker. Typical galvanized coatings range from 3-8 mils (75-200 microns). When designing and detailing tapped holes, the increased thickness is important. Hole sizes in certain fabricated steel products must be oversized to account for the zinc that bonds to the edges. If after galvanizing the hole is still not large enough, it can be retapped. Retapping will not necessitate regalvanizing. Because of the zinc coating's cathodic properties, the coating on the mating fastener will protect chased or retapped nuts. For holes that will be threaded after galvanizing, the hole should be drilled undersize before galvanizing so the threads can be cut after galvanizing.

Threaded Assemblies

Best practice suggests that studs and bolted assemblies be sent to the galvanizer disassembled.

Threaded fasteners are galvanized in baskets. Once removed from the kettle, excess zinc is then spun off the fasteners in a centrifuge.

On threaded assemblies with diameters greater than 1.5 inches (1.8 cm), it is often more practical, if design strength allows, to have the male thread cut 0.031" (0.8 mm) undersize before galvanizing so a standard tap can be used on the nut. Low carbon and low silicon bars are recommended as the fastener material to be galvanized, since high carbon and silicon levels cause heavier, rougher galvanized coatings. Sharp manufacturing tools should be used to minimize the possibility of ragged and torn threads opening up during the cleaning phase of the galvanizing process. Standard-sized threads are cut on the bolt, while standard-sized nuts are re-tapped oversize after galvanizing to allow for the dimensional increase of the threads from the zinc coating. Because of the zinc coating's cathodic properties the zinc coating on the mating bolt threads will protect the chased or retapped nuts.

Venting and Drainage

In the hot-dip galvanizing process, steel is completely coated with corrosion-inhibiting zinc, which forms a highly abrasion-resistant metallurgical bond with the base steel. In order to ensure that all interior and exterior surfaces are protected from corrosion, entire steel fabrications are dipped in cleaning solutions, flux solutions, and molten zinc metal. In order to facilitate interior and exterior cleaning and coating, it is necessary to provide holes in fabrications to be galvanized. The primary reason for vent and drain holes is to allow air to be evacuated from within and around the fabrication, allowing it to be completely immersed in the cleaning solutions and molten zinc and for the excess zinc and solutions to drain out and away from the part.

Drain and vent holes need to be placed in the correct locations on any closed pieces. When air becomes trapped in tubing, pipe or in blind areas, the expansion of the trapped air can result in a dangerous situation that can injure galvanizing personnel and/or damage the product.

The secondary reason is if fabrications to be galvanized are not properly vented, trapped cleaning solutions or rinse waters may flash into steam. The resulting pressure increase (up to 3600 psi [25MPa]) can rupture the fabrication. Additionally, trapped moisture that flashes to steam can result in localized uncoated surfaces. For the same reason overlapping or contacting surfaces should be seal welded to prevent trapping of the cleaning solutions. Because items being galvanized are immersed in and withdrawn from all cleaning solutions and molten zinc at an angle, vent holes should be located at the highest point and drain holes at the lowest point as mounted during the galvanizing process.

Post-Treatments

Galvanized steel is used for many different applications in a variety of environments. Post treatments are applied to galvanized steel to enhance the corrosion protection, or change the appearance of the zinc coating and other properties as follows:

- Tension leveling or roller leveling to improve flatness
- Skin passing to make the surface smoother and to minimize yield-point behavior
- Overaging heat treatment to improve mechanical properties
- Slitting to narrower widths, shearing to produce cut lengths of sheet, and side trimming to remove nonuniform edges
- Chromate passivating to provide temporary protection against corrosion during shipment and storage
- Oiling to provide lubricity during forming
- Oiling to provide temporary corrosion protection during shipment and storage
- Phosphating to improve formability

As listed above, post treatments are commonly used to passivate the zinc surface to inhibit the formation of corrosion products during transportation or storage. If galvanized steel is tightly packed and humid and/or wet conditions exist, its zinc coating tends to form voluminous white corrosion products. This build-up is typically superficial and weathers away shortly after the steel is put in service. However, extreme build-up in very humid or wet environments may be detrimental to the overall corrosion protection provided by the hot-dip galvanized coating. The corrosion products can easily be removed using a nylon-bristled brush and an alkaline-based cleaner. Passivating the surface of the hot-dip galvanized steel will provide added short-term corrosion protection to prevent against excessive build-up of corrosion products. Hot-dip galvanized material may be stacked with wood spacers in between pieces to promote free flowing air and reduce the potential of forming voluminous white corrosion products. Chromate treatments are used on galvanized steel products to prevent the formation of wet storage stain during the first weeks after galvanizing. The zinc coating is most vulnerable to the formation of excessive amounts of zinc oxide and zinc hydroxide during this period. The thin layer of chromate passivation layer inhibits the formation of these zinc oxides. Passivation by this method is done by spray or dip application of an acid chromate solution, removing excess solution by use of squeegee rolls, and drying the residue in hot air. Given the increasing environmental concerns about chromium, particularly in the hexavalent form, this type of chemical passivation is slowly being phased out.

Paint or powder coatings are commonly applied to the surface of galvanized articles to extend the corrosion protection life of the article. The use of dual corrosion protection materials is often called "duplex" systems. The synergistic effect of the two coatings produces service lifetimes greater than those anticipated by the sum of the separate material service lifetimes. Painting may also be required for aesthetic or safety reasons. Chemical plants often require the color-coding of pipes and process units to warn operators of potential dangers. Therefore, if a designer specifies pieces of equipment to be galvanized, the hot-dip galvanized coating must be readily paintable and the subsequent steps to prepare the surface for painting must be implemented. In order to achieve good paint adhesion, it is important that the surface is properly pretreated. Zinc phosphate or complex oxide pretreatments are the usual for coil-line prepainted sheet. For galvanized components that are painted after fabrication, such as automobile body components, zinc phosphate or zinc phosphates modified with nickel or manganese are commonly used.

Water quenching is commonly used in the galvanizing industry as a method of cooling newly galvanized steel after it has been removed from the kettle. The water quench is generally comprised of water and/or mild soaps to which passivation agents may be added to provide some short-term protection against the formation of corrosion products.

A normal galvanized coating often has a bright shiny finish that most specifiers find aesthetically pleasing. However, in some applications, the surface reflectivity of galvanized steel is a concern. Land management agencies and forest services often require galvanized structure surfaces to be dulled so as to blend with the surroundings. Galvanized structures found along roads and highways are dulled for safety reasons.

Inspection

Two properties of the hot-dip galvanized coating that are closely scrutinized after galvanizing are coating thickness and coating appearance. As mentioned in the previous sections, a variety of simple physical and laboratory tests may be performed to determine thickness, uniformity, adherence, and appearance. Inspection of the galvanized product is most effectively and efficiently conducted at the galvanizer's plant. Here, questions and concerns can be raised and dealt with quickly and efficiently, speeding up the inspection process and resulting in a time savings that is an asset to the overall project.

For large articles such as plates, bars, and angle sections, tests should be conducted on the galvanized article according to the procedure described in ASTM A123. The measurement of coating thickness should be taken at widely-dispersed points to represent a true sampling of the whole part. Extremely large parts may need to be tested in sections in order to represent the entire product.

The most common method for measuring the coating thickness of hot-dip galvanized steel is by using magnetic thickness measurements in accordance with ASTM E376. A minimum of five readings should be taken for each specimen. The average of the thickness values taken for each specimen should not be less than one coating thickness grade lower than the value listed in the appropriate specification.

The hot-dip galvanized coating on a steel sheet or bar must withstand bending without flaking or peeling when the bending test is preformed in accordance with the applicable ASTM product specification. There are various tests used to assess the ductility of steel when subjected to bending. The most common type is to determine the minimum radius or diameter that the material can withstand without failure when it is bent through a given angle and over a definite radius.

Chromating is commonly performed on zinc-plated parts to make them more durable. The chromate coating acts like paint, protecting the zinc from white corrosion, this can make the part several times more durable depending on chromate layer thickness. The specification to determine the presence of chromate on zinc surfaces is ASTM B201. This test involves placing drops of a lead acetate solution on the surface of the product, waiting 5 seconds, and then blotting it gently. If this solution creates a dark deposit or black stain, then there is unpassivated zinc present. A clear result indicates the presence of a chromate passivation coating.

Products are galvanized according to long-established, well-accepted and approved standards of the American Society of Testing and Materials International (ASTM), the Canadian Standards Association (CSA), and the American Association of State Highway and Transportation Officials (AASHTO). These standards cover everything from the minimum required coating thicknesses for various categories of galvanized items to the composition of the zinc metal used in the process.

Related Specifications

American Society for Testing & Materials (ASTM International)
ASTM A123, Specification for Zinc (Hot-Dip Galvanized) Coatings on Iron and Steel Products
ASTM A143, Practice for Safeguarding Against Embrittlement of Hot-Dip Galvanized Structural Steel Products and Procedure for Detecting Embrittlement
ASTM A153, Specification for Zinc Coating (Hot-Dip) on Iron and Steel Hardware
ASTM A384, Practice for Safeguarding Against Warpage and Distortion During Hot-Dip Galvanizing of Steel Assemblies
ASTM A385, Practice for Providing High Quality Zinc Coatings (Hot-Dip)
ASTM A767, Specification for Zinc-Coated (Galvanized) Steel Bars for Concrete Reinforcement
ASTM A780, Practice for Repair of Damaged and Uncoated Areas of Hot-Dip Galvanized Coatings
ASTM B6, Specification for Zinc
ASTM B201, Standard Practice for Testing Chromate Coatings on Zinc and Cadmium Surfaces
ASTM D 6386, Practice for Preparation of Zinc (Hot-Dip galvanized) Coated Iron and Steel Product and Hardware Surfaces for Painting
ASTM E376, Measuring Coating Thickness by Magnetic-Field or Eddy-Current (Electromagnetic) Test

Methods

CORROSION PERFORMANCE-ATMOSPHERIC CORROSION

The corrosion rate of zinc is directly influenced by atmospheric conditions. Certain factors that specifically affect the corrosion of zinc include: temperature, humidity, rainfall, sulfur dioxide (pollution) concentration in the air, and air salinity. None of these factors can be singled out as the main contributor to zinc corrosion, but they all play a role in determining the corrosion protection that hot-dip galvanized coatings can provide in certain environments.
For corrosion classification purposes, atmospheres are generally divided into five groups:

Industrial Atmosphere: Power Plant

Industrial Atmospheres: These environments are generally the most aggressive in terms of corrosion. Air emissions may contain some sulfides and phosphates that cause the most rapid consumption of the zinc coating. Automobiles, trucks and industrial plant exhaust are examples of these emission sources. Most city or urban area atmospheres are classified as industrial with the most aggressive conditions often found in places of intense industrial activity where the coating is frequently wetted by rain, snow and other forms of condensation. In these areas, sulfur compounds can combine with atmospheric moisture to convert the normally adherent and insoluble zinc carbonates into zinc sulfite and zinc sulfate. These sulfur compounds are water-soluble and adhere poorly to the zinc surface. They are removed by rain with relative ease, exposing a fresh zinc surface to additional corrosion.

Suburban Atmosphere

Suburban Atmospheres: These atmospheres are generally less corrosive than industrial areas and, as the term suggests, are found in the largely residential, perimeter communities of urban or city areas with little or no heavy industry.

Temperate Marine: Dock System

Temperate Marine Atmospheres: The service life of the galvanized coating in marine environments is influenced by proximity to the coastline and prevailing wind direction and intensity. In marine air, chlorides from sea spray can react with the normally protective zinc corrosion products to form soluble zinc chlorides. When these chlorides are washed away, fresh zinc is exposed to corrosion. Nevertheless, temperate marine atmospheres usually are less corrosive than suburban atmospheres.


Tropical Marine: Bridge by the Ocean

Tropical Marine Atmospheres: These environments are similar to temperate marine atmospheres except they are found in warmer climates. Tropical marine climates tend to be somewhat less corrosive than temperate marine climates, because many tropical areas are found relatively far removed from moderately industrial areas.

Rural Atmosphere: Grain Silo

Rural Atmospheres: These are usually the least aggressive of the five atmospheric types. This is primarily due to the relatively low level of sulfur and other emissions found in such environments.
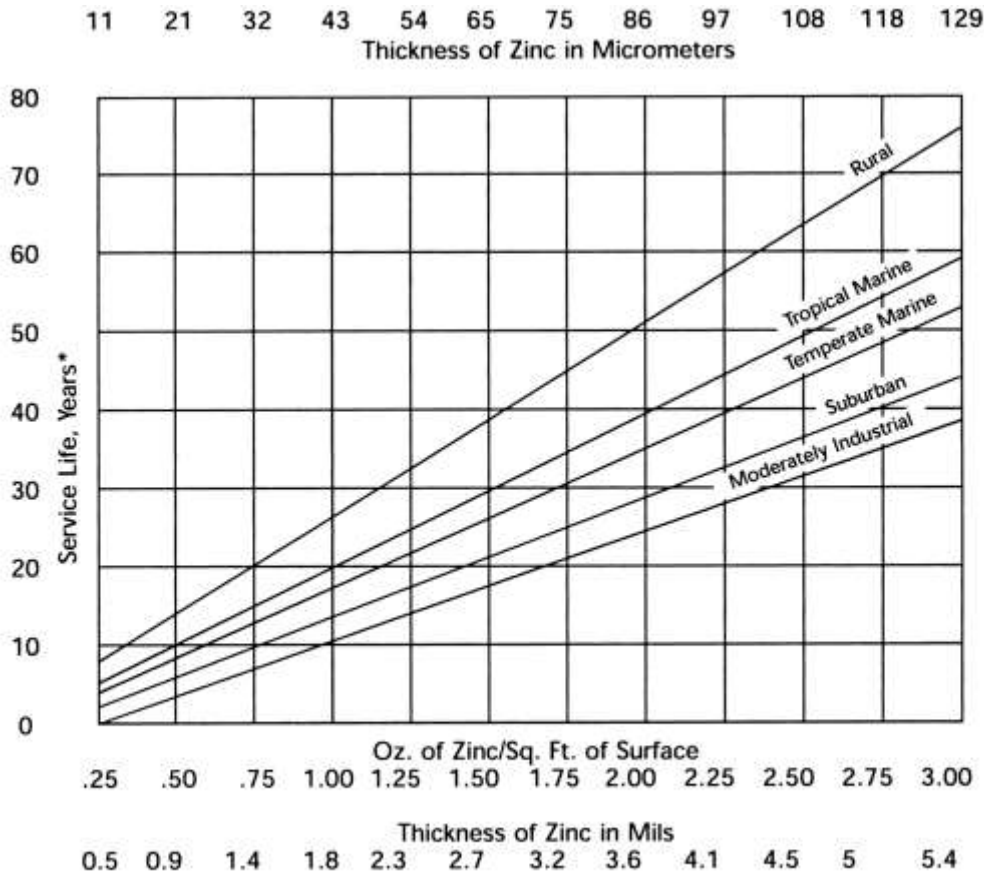
*Service Life is defined as the time to 5% rusting of the steel surface.

1 mil=25.4µm=0.56 oz/ft²

The chart located above is a plot of the galvanized coating thickness against the expected

service life of the coating under outdoor exposure conditions. These curves were generated by the Zinc Corrosion Life Predictor software (available at the American Galvanizers Association website). The program performs calculations based on models that were developed using statistical methods, neural network technology and an extensive worldwide corrosion database.

The corrosion rates of zinc have decreased over the past 30 years due to the efforts of environmental policies and industrial improvements that have resulted in a cleaner environment. Restrictions on the exhaustion of harmful chemicals and improvements in fume capture and exhaust air controls, as well as fuel changes, have significantly improved air quality and reduced pollution levels. By reducing pollution levels - or corrosive elements in the air - the corrosion rate of metals, particularly zinc, also decreased.

Expected service life is defined as the life until 5% of the substrate surface is showing iron oxide (rust). At this stage, it is unlikely that the underlying steel or iron has been weakened or the integrity of the structures protected by the galvanized coating otherwise compromised through corrosion. An appropriately selected corrosion protection system such as zinc-rich paint, zinc metal spray, or zinc solder may be used to repair the exposed area.

Zinc oxide is the initial corrosion product of zinc when exposed to air after galvanizing. Zinc oxides are formed by a reaction between the zinc and atmospheric oxygen. In the presence of moisture, zinc oxide is converted to zinc hydroxide. Zinc hydroxide and zinc oxide further react with carbon dioxide in the air to form zinc carbonate. The zinc carbonate film is tightly adherent and relatively insoluble and is known as the "zinc patina". It is primarily responsible for the excellent and long-lasting corrosion protection provided by the galvanized coating in most atmospheric environments.

Since 1926, ASTM Committees A05 (Metallic Coated Iron and Steel Products) and G01 (Corrosion of Metals), and other organizations have been collecting continuous records of the behavior of zinc coatings under various atmospheric conditions. These atmospheric exposure tests have been conducted throughout the world to obtain corrosion rate data for zinc. Precise comparison of the corrosion behavior of the galvanized coating in various atmospheric environments is influenced by many factors, including prevailing wind direction, type and density of corrosive fumes and pollutants, amount of sea spray, number of wetting and drying cycles, and the duration of exposure to moisture. Although there is a range in observed corrosion rates, actual observed rates rarely exceed 0.3 mils (0.0003") per year. It is also worthwhile to note that when exposed indoors, the life of the galvanized coating will be at least two to three times that expected with outdoor exposure in the same location.

The Corrosion Process

Metals are rarely found in their elemental form in nature. They most frequently are found in chemical combination with one or more nonmetallic elements. Ore is generally an oxidized form of metal that is mined to produce pure metals. Significant energy must be input to reduce the ore to a pure metal. This energy can be applied via metallurgical or chemical means. Additional energy also may be input in the form of cold-working or casting to transform the pure metal into a working shape. Corrosion can be viewed as the tendency for a metal to revert to its lowest energy state. From a thermodynamic perspective, the tendency to decrease in energy is the main driving force for the corrosion of metals.

Unprotected steel will begin to corrode immediately once exposed to environment

Corrosion of metals is an electrochemical process. That is, metal corrosion involves both chemical reactions and the flow of electrons. A basic electrochemical reaction that drives the corrosion of metals is galvanic action. In a galvanic cell, current is generated internally by physical and chemical reactions occurring among the components of the cell.

Galvanic Corrosion

There are two primary types of galvanic cells that cause corrosion: the bimetallic couple and the concentration cell. A bimetallic couple is like a battery, consisting of two dissimilar metals acting as electrodes immersed in an electrolyte solution. An electric current (flow of electrons) is generated when an external continuous metallic path connects the two electrodes. A concentration cell consists of an anode and cathode of the same metal or alloy and a return current path. The electromotive force is provided by a difference in concentration of the solutions contacting the metal(s). In a galvanic cell, there are four elements necessary for corrosion to occur:
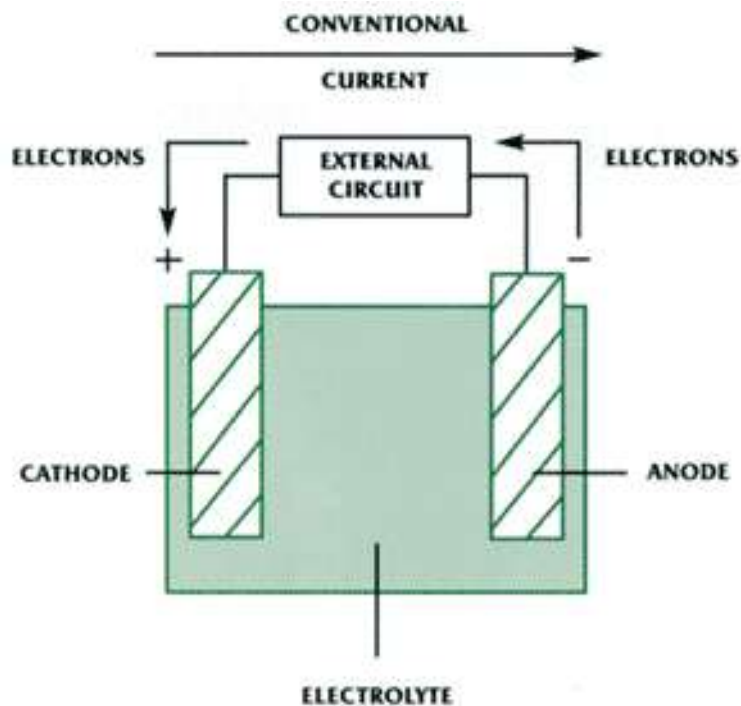
A Corrosion cell consists of four elements and can exist in various sizes

Anode: This is the electrode where the anode reaction generates electrons. Corrosion occurs at the anode.
Cathode: This is the electrode that receives electrons. The cathode is protected from corrosion.
Electrolyte: This is the conductor through which ion current is carried. Electrolytes are primarily water solutions containing salts, metals, and other elements.
Return Current Path: This is a metallic pathway connecting the anode to the cathode. It is often the underlying metal.

These four elements constitute the basic galvanic corrosion cell. As a result, the protection system must concentrate on these elements. Removing any one of these elements will stop the current flow and corrosion will not occur. Substituting a different metal for the anode or cathode may cause the direction of the current to reverse, resulting in a change as to which electrode experiences corrosion. This substitution of one metal as the corrosion material is called galvanic protection. It is possible to construct a table of metals and alloys listed in decreasing order of electrical activity. Metals nearer the top of the table often are referred to as less noble metals and have a greater tendency to lose electrons than the more noble metals found lower on the list. The less noble metals are used as corrosion protection materials. This table is known as the galvanic series (shown below).

Galvanic series in seawater at 25 °C (77 °F)

Corroded end (anodic, or least noble)

Magnesium
Magnesium alloys
Zinc
Galvanized steel or galvanized wrought iron
Aluminum alloys
5052, 3004, 3003, 1100, 6053, in this order
Cadmium
Aluminum alloys
2117, 2017, 2024, in this order
Low-carbon steel
Wrought iron
Cast iron
Ni-Resist (high-nickel cast iron)
Type 410 stainless steel (active)
50-50 lead-tin solder
Type 304 stainless steel (active)
Type 316 stainless steel (active)
Lead
Tin
Copper alloy C28000 (Muntz metal, 60% Cu)
Copper alloy C67500 (manganese bronze A)
Copper alloys C46400, C46500, C46600, C46700
    (naval brass)
Nickel 200 (active)
Inconel alloy 600 (active)
Hastelloy alloy B
Chlorimet 2
Copper alloy C27000 (yellow brass, 65% Cu)
Copper alloys C44300, C44400, C44500
    (admiralty brass)
Copper alloys C60800, C61400 (aluminum bronze)
Copper alloy C23000 (red brass, 85% Cu)
Copper C11000 (ETP copper)
Copper alloys C65100, C65500 (silicon bronze)
Copper alloy C71500 (copper nickel, 30% Ni)
Copper alloy C92300, cast (leaded tin bronze G)
Copper alloy C92200, cast (leaded tin bronze M)
Nickel 200 (passive)
Inconel alloy 600 (passive)
Monel alloy 400
Type 410 stainless steel (passive)
Type 304 stainless steel (passive)
Type 316 stainless steel (passive)
Incoloy alloy 825
Inconel alloy 625
Hastelloy alloy C
Chlorimet 3
Silver
Titanium
Graphite
Gold
Platinum

Protected end (cathodic, or most noble)

The actual corrosion process that takes place on a piece of bare mild steel is very complex due to factors such as variations in the composition/structure of the steel, presence of impurities due to the higher instance of recycled steel, uneven internal stress, and exposure to a non-uniform environment.It is very easy for microscopic areas of the exposed metal to become anodic or cathodic. A large number of such areas can develop in a small section of the exposed metal. Further, it is highly possible that several different types of galvanic corrosion cells are present in the same small area of the actively corroding piece of steel.
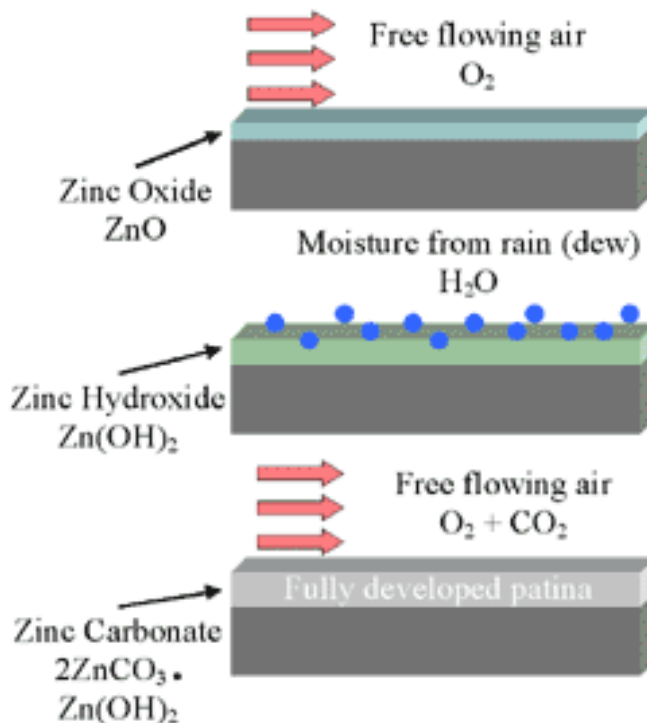
As the corrosion process progresses, the electrolyte may change due to chemical changes on the surface of the steel. Additionally, corrosion products tend to build up on certain areas

of the metal. These corrosion products do not occupy the same position in the given galvanic series as the metallic component of their constituent element. As time goes by, there may be a change in the location of relatively cathodic and anodic areas and previously uncorroded areas of the metal are attacked and corrode. This eventually will result in uniform corrosion of the entire area. The rate at which metals corrode is controlled by factors such as the electrical potential and resistance between anodic and cathodic areas, pH of the electrolyte, temperature, and humidity.

Zinc Patina/Handling and Storage

Freshly galvanized steel progresses through a natural weathering process. During the first few weeks following galvanization, the zinc coating develops a natural protective patina. If allowed to develop naturally, the patina itself provides an inert corrosion protection layer for the active zinc metal.

Formation of the zinc patina begins with the exposure of freshly galvanized steel to atmospheric oxygen. Initially, a thin layer of zinc oxide develops on the surface of the steel as a result of the zinc metal and oxygen reacting. This oxide layer continues to react with water, rainfall, or dew, to form a porous, gelatinous zinc hydroxide. During drying, this product reacts with carbon dioxide present in the atmosphere and converts into a thin, compact, and tightly adherent layer of corrosion products consisting mainly of basic zinc carbonate. The rate of patina formation varies according to the environmental conditions. Typically, it takes 6 - 12 months to fully develop.

Free flowing air
O_2

Zinc Oxide
ZnO

Moisture from rain (dew)
H_2O

Zinc Hydroxide
$Zn(OH)_2$

Free flowing air
$O_2 + CO_2$

Fully developed patina

Zinc Carbonate
$2ZnCO_3 \cdot Zn(OH)_2$

Formation cycle of the zinc patina

Research and corrosion testing have shown that zinc's ability to provide long-term corrosion protection is mainly based on the formation of the zinc patina. This relatively insoluble layer of zinc corrosion products inhibits the formation of new corrosion products by acting as a barrier to the underlying galvanized coating. The patina also heals itself upon damage by reforming the corrosion products when fresh zinc metal is exposed to the atmosphere.

Handling and storage conditions can inhibit the formation of the patina. Storage areas that are high in humidity and lack air circulation tend to produce excessive growth of zinc oxide and zinc hydroxide. Adequate ventilation must be provided insuring that the build-up and retention of excessive water on the surface of the galvanized article does not occur. Tightly contacting pieces do not allow for air to flow freely across the galvanized surface, limiting the amount of carbon dioxide that is available for the formation of the zinc carbonate layer.

Galvanized articles should be stacked so that tight contact between pieces is avoided and collected water is allowed to drain. However, light to medium coatings of zinc oxide and zinc hydroxide will not detrimentally affect the corrosion protection of zinc. If an article with a light to medium zinc oxide and zinc hydroxide layer is exposed to the atmosphere, the layers will be converted into the protective layer of zinc carbonate as shown above. Only heavy build-up of voluminous zinc oxide and zinc hydroxide must be removed to ensure the corrosion protection of the product is not significantly reduced.

Chemical Corrosion

A primary factor governing corrosion behavior of metallic coatings in liquid chemical environments is the pH of the chemical solution. Galvanizing performs well in solutions of pH above 5.5 and below 12.5 as shown in figure below. This should not be considered a hard and fast rule, because factors such as agitation, aeration, temperature, polarization, and the presence of inhibitors may affect the rate of corrosion.

Within the pH range of 5.5 - 12.5, a protective film forms on the zinc surface and the corrosion rate is very slow. The exact chemical composition of the protective film is somewhat dependent upon the specific chemical environment. Since many liquids fall within the pH range of 5.5 - 12.5, galvanized steel containers are widely used in storing and transporting many chemical solutions.
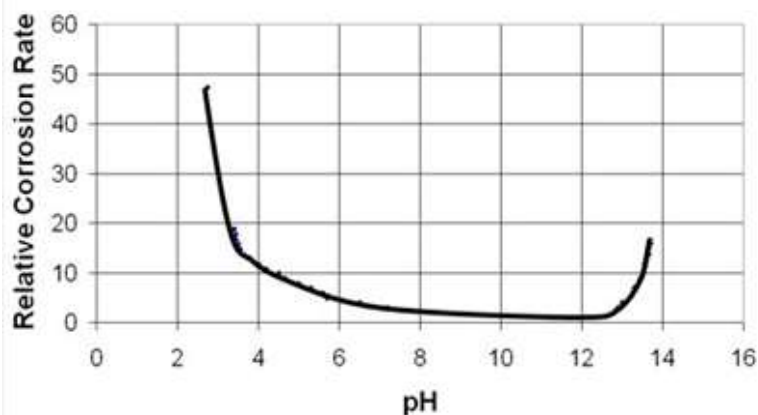
Corrosion Rate of Zinc versus pH

Water Corrosion

The varieties of water throughout the world differ to the extent that predicting corrosion rates is very difficult for all coatings. Many parameters affect corrosion of metals in a water environment, including pH level, oxygen content, water temperature, water climate and tide conditions, to name a few. Despite the difficulty of predicting corrosion, it is important to note that galvanized coatings on steel used in submersed applications is still one of the best methods of corrosion protection. It is common for hot-dip galvanized steel to perform flawlessly in harsh water environments such as seawater for 8 to 12 years.

Hot-dip galvanized sprinkler systems provide corrosion protection for many years

The first step in deciding whether galvanized steel is the right coating for your application is to determine what type of water will be used. Water is typically pure water (e.g., distilled water or de-ionized water), natural fresh water, potable water (treated drinking water), or seawater. Hard water and soft water also cause corrosion to different degrees, as do hot and cold water. A marked increase in rates of corrosion occurs at a temperature of about 140°F (60°C), followed by a decrease in corrosion at higher temperature. At temperatures near 160°F (70°C) a reversal of potential may occur where zinc coatings become cathodic to iron. This may be of interest because of major use of galvanized steel in hot water systems.

Pure Water

Pure water, also known as de-ionized or distilled water, does not corrode zinc severely, provided it is free from oxygen and carbon dioxide. Even upon exposure to pure water with uniform oxygen content, the attack of pure water on zinc isn't very pervasive. However, even though corrosion may be minimal in pure water, light to severe pitting may occur. Corrosion rates of steel increase with aeration of pure water; dissolved oxygen in pure water is five to ten times more aggressive than carbonic acid.

Natural Fresh Water

Fresh water environments have two major constituents for categorizing corrosion potential: hard and soft water. Carbonates and bicarbonates, present in some concentration in fresh water, tend to deposit protective films on the zinc surface, helping to stifle corrosion. Carbonates subdue the corrosion effects of anions, the most corrosive to zinc being chloride in excess of 50 mg/L. The softer the water, the lower it is in carbonate, which means a more pronounced chloride content. Conversely, the harder the water the greater it is in carbonate and the corrosiveness of the chlorides are minimized. Therefore, the general rule is that the corrosion rate of soft water is higher than hard water.

Sea Water

Seawater is high in salt content in the form of various chlorides. Typical surface seawater has a pH of 8 due to excess amounts of carbonates. The pH may fall to 7 in stagnant waters. The depth of the water also plays a part in the pH level. The pH decreases with depth. Corrosion of zinc is best controlled in the pH range of 5.5 to 12. Seawater temperature can vary widely from 28°F (-2°C) at the poles to (95°F) 35°C near the Equator. The higher the temperature the greater the dissolution of zinc in water. Tropical seawater (higher temperatures) yields higher corrosion rates, especially in polluted waters.

Potable Water

The Clean Water Act, which includes the Drinking Water Standard, requires that any material or coating that comes in contact with drinking water must be tested. The EPA contracted the National Sanitation Foundation (NSF) to write the test procedure, which after many drafts and public meetings, was finally published as NSF Standard 61: "Drinking Water Systems Components: Health Effects". Therefore, only galvanizers that have submitted test coupons of their galvanized steel and have been approved by the NSF have the authority to galvanize steel for use with potable water.

Causes of Zinc Corrosion in Water

Determining the corrosion rate of zinc in water can be quite complicated. Below is the summary of the basic elements that cause the corrosion of zinc:

- Soft water is a harsher environment (up to 10 times the corrosion rate) to zinc than is hard water or even cold climate seawater.
- Temperate seawater deposits protective scales on zinc and is less corrosive than soft water.
- High oxygen content and warm waters can be detrimental to zinc as well.
- Corrosion of zinc is lowest in the pH range from about 5.5 to 12.5. However, the corrosion of zinc in water is accelerated largely by the impurities present in the water and rarely is natural water pure. Even rainwater, which is distilled by nature, contains nitrogen, oxygen, carbon dioxide, as well as acquired airborne impurities such as dust or smoke.
- Anything that disturbs the formation of a protective film on the zinc surface will inhibit the hot-dip galvanized coating from delivering superior corrosion protection. In addition, other factors including time of exposure, temperature, and fluid agitation all influence the corrosion of zinc in water.

Corrosion in Soils

The corrosion of bare steel in soils varies significantly based on the type and location of the soil. The corrosion rate of steel in soil can range from less than 20 microns per year (0.8 mil/year) in favorable conditions, to 200 microns per year or more in very aggressive soils. Thus, highly corrosive soils will dictate the need for a reliable corrosion protection system to ensure long-term protection. In numerous types of soils, hot-dip galvanizing can provide the necessary corrosion protection to extend the life of the steel by many years.

Predicting soil corrosivity is a daunting task that begins with classification of the soil. Due to the varying physical and chemical characteristics of soil, it is extremely difficult to predict underground corrosion rates. Even in very close proximity, soil content conditions can have significant variations. In order to predict the performance of hot-dip galvanized steel in soil, you must first try to classify the soil in which the steel will be embedded. The properties of soil that have the most effect on the corrosion rate of zinc are aeration, moisture content (or time of wetness), pH, temperature, and resistivity.

Generally speaking, sandy, well-aerated soils with a neutral or slightly basic pH are likely to cause only limited corrosion of zinc, most likely below ten microns per year (0.4 mil/year). One of the easiest ways to view soil classification is through color. Red, yellow, or brown soil indicates the presence of oxidized iron that corresponds to soil that is well aerated. Soils that are gray indicate that it is poorly aerated and are generally more corrosive to zinc. Particle

size plays a very large role in determining the longevity of hot-dip galvanizing in a particular soil. Particle size will dictate the amount of aeration as well as the time of wetness for contacting galvanized steel. Soil particle sizes are generally divided into three categories: sand (0.07 - 2 mm), silt (0.005 - 0.07 mm), and clay (< 0.005 mm). In sandy soils, the larger particle size allows for air to enter between the particles and promote aeration of the soil. At the same time, aerated soils allow moisture that remains in the soil from rainfall or other sources to evaporate at a much faster rate than non-aerated soils of smaller particle size. This resulting aeration and shorter time of wetness correlates to a lower corrosion rate of zinc.

High levels of bacteria in the soil tend to consume any oxygen present, thus making the soil poorly aerated. Hot-dip galvanized steel will not perform as well in soils containing large amounts of organic bacteria.

Soils also have a wide range of chemical properties, as well as physical properties, that make it difficult to predict corrosion rates of zinc. Studies have shown that the pH of soil can vary from 2.6 up to 10.2. As with galvanized steel in contact with solutions, the pH has a dramatic affect on the corrosion rate of zinc. Hot-dip galvanized steel performs the best in soils that are neutral or slightly basic. Extreme corrosion rates and deep pitting are associated with soils having very low pH (highly acidic).

Plentiful rainfall typically translates into soils that are more acidic and are more corrosive to zinc. Also, rainfall affects the time of wetness for the soil and the contacting galvanized parts. The longer that the galvanized steel remains wet, the higher the corrosion rate.

Temperature also plays a role in the rate at which corrosion of galvanized steel in soil occurs. One study has shown that the corrosion rate doubles in samples when the temperature was raised from 40 - 68°F (4 - 20°C). The lower temperature results in a higher resistivity of the soil. Some studies have shown corrosion rates are lower in soils with high resistivities, however, a good correlation between resistivity and corrosion rates does not exist. In summary, hot-dip galvanized steel extends the service life of steel covered by soil. Predicting how much longer the galvanized coating will extend the life of the steel is an inexact science and requires the gathering of multiple soil characteristics.

Corrosion in Concrete

Repairing damage caused by corrosion is a multi-billion dollar problem. Observations of numerous structures show that corrosion of reinforcing steel is either a prime factor, or at least an important factor, contributing to staining, cracking and/or spalling of concrete structures. The effects of corrosion often require costly repairs and continued maintenance during the life of the structure.

Under normal conditions, concrete is alkaline (pH of about 12.5) due to the presence of calcium hydroxide. In such an environment, a passivating iron-oxide film forms on the steel, causing almost complete corrosion inhibition. As the pH of the concrete surrounding the reinforcement is reduced by the intrusion of salts, leaching, or carbonation, the system becomes active and corrosion proceeds.
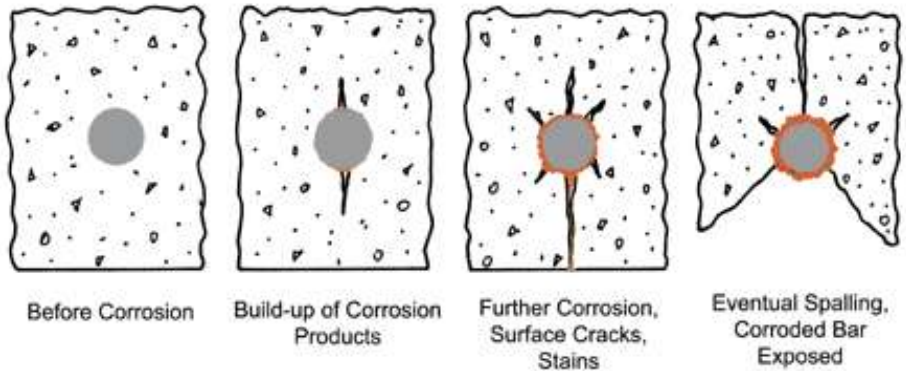
The presence of chloride ions can affect the inhibitive properties of the concrete in two ways. The presence of chloride ions creates changes in the iron oxide, resulting in pitting corrosion. Carbonation can lower the pH and increase the corrosion rate. Any additional changes in pH will accelerate the bare steel corrosion rate. The iron corrosion products that form on steel have much greater volume than the metal that is consumed in the corrosion reaction. This increase in volume around the bare steel rebar exerts great disruptive tensile stress on the surrounding concrete. When resultant tensile stress is greater than the concrete tensile

strength, the concrete cracks (as shown in the figure below), leading to more changes by allowing rain and chlorides direct access to the steel bar. Corrosion cracks are usually parallel to the reinforcement and are quite distinct from transverse cracks associated with tension in the reinforcement caused by loading. As the corrosion proceeds, the longitudinal cracks widen and, together with structural transverse cracks, cause spalling of the concrete.

Concrete cannot survive the outward pressure produced by steel corrosion products, which expand significantly and cause cracking of the concrete. As corrosion progresses the concrete can completely fracture away from the rebar causing spalling.

Galvanized reinforcing steel is effectively and economically used in concrete where unprotected reinforcement will not have adequate durability. The susceptibility of concrete structures to the intrusion of chlorides is the primary incentive for using galvanized steel reinforcement. Galvanized reinforcing steel is especially useful when the reinforcement will be exposed to the weather before construction begins. Galvanizing provides visible assurance that the steel has not rusted and requires no on-site repair, unlike most other coatings. Galvanized reinforcing steel retards corrosion, providing barrier and sacrificial protection. As the corrosion products of zinc are much less voluminous than those of steel, the cracking, delamination, and spalling cycle illustrated below is greatly reduced when using galvanized rebar.

Before Corrosion   Build-up of Corrosion   Further Corrosion,   Eventual Spalling,
                          Products   Surface Cracks,   Corroded Bar
                                                         Stains   Exposed

Corrosion in Chemical Environments

Zinc is usually not considered to be a useful protection for acidic or strongly alkaline environments, for example in chemical process industries. Its corrosion rate increases rapidly in aqueous chemical solutions on either side of the 6 to 12 pH range. This however, should not be considered as a fixed rule, because many other factors, such as agitation, aeration, temperature, polariziation, and in some cases, the presence of inhibitors, may have considerable influence on the corrosion.

There is considerable interest in the use of zinc in milder chemical environments. For example, zinc is used in contact with many organic chemical and chemical specialties such as detergents, insecticides, agricultural chemicals and similar materials. In most cases, zinc comes in contact with such chemicals during handling, packaging and storage of commercial products.
Usually the corrosion resistance of zinc to the chemicals is the major consideration, but in some cases, the effect of zinc corrosion on a consumer product or chemical is of greater concern than the actual corrosion rate of zinc.