

Hot Dip Galvanized Information Sheet No.6

Corrosion Control by Hot Dip Galvanized Steel in Water

Hot Dip Galvanizing

As the name implies, the application of the zinc coating is a hot dipping process whereby cleaned carbon steel is immersed into molten zinc at a temperature of between 445°C and 450°C. When perfectly cleaned steel is immersed into molten zinc, a chemical reaction, governed by “metallurgical laws” will result in the formation of tenacious zinc and / or zinc iron alloy coating. Figure One is a micrograph of such a coating applied to a sample of “aluminium killed” steel. The adhesion of the coating to the carbon steel is by means of a metallurgical bond, which is considered to be far superior to that of any mechanical bond. Typically, the service life of a hot dip galvanized coating is proportional to its thickness. The thicker the zinc coating, the longer the service life.”

The characteristics of a hot dip galvanized coating are summarized as follows.

- Relatively uniform and can range from a bright silvery to a dull gray surface finish, depending on the chemical analysis of the steel being processed.
- Coating thickness usually between 55 to >100 microns (μm), depending on steel thickness as well as the chemical composition of the steel being processed.
- The coating consists of a series of zinc / iron layers, the formation of which are influenced by the chemical composition of the steel being processed.
- Zinc is electro-negative to carbon steel and will therefore provide “cathodic protection” to the steel should small uncoated surface imperfections arise.

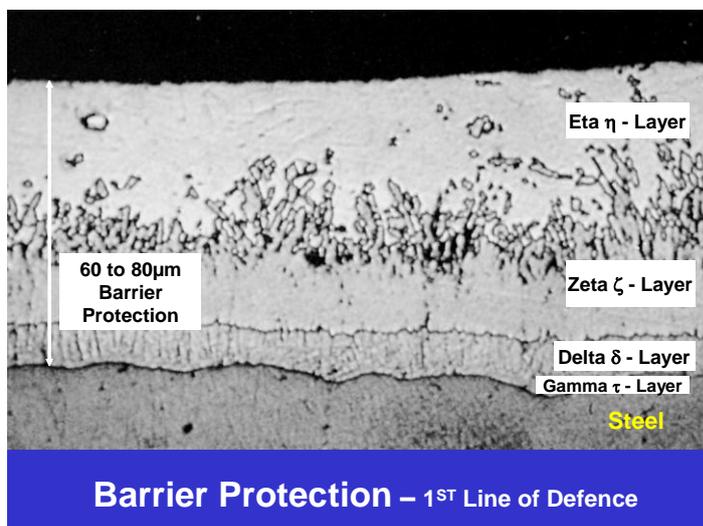


Figure 1: Micrograph (x200) of a typical Hot Dip Galvanized coating on “Aluminum Killed Steel”

Protective Characteristics of Hot Dip Galvanized Coatings Immersed in Water

Natural ground water absorbs soluble salts as chlorides and sulphates. In addition, the use of modern chemicals in fertilisers, can add nitrates and phosphates to rivers. The level of acidity of water results from the amount of dissolved carbon dioxide absorbed from the atmosphere. Similarly other soluble gases (such as oxygen, sulphur dioxide – so called acid rain and hydrogen sulphide) can be absorbed by water.

Therefore all ground waters encountered in nature are impure containing varying levels of chemicals and dissolved gases. Drinking water standards place tolerable limits on the level of these substances. All materials, employed for purposes of corrosion control, have distinctive characteristics in their reaction to the various ground waters encountered in nature. Hot dip galvanized coated carbon steel is no exception.

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The following parameters are generally required to assess the corrosivity of water.

Table No. 1 Typical Water Analysis

Parameter	Unit	Typical Values	Corrosive	Mild	Benign
Temperature	° C	20			
PH		7 to 7½	<5½ & >12½	6 to 8	8 to 12
Chlorides (as Cl)	mg/l	<50			
Sulphates (as SO ₃)	mg/l	<5			
Alkalinity (as CaCO ₃)	mg/l	15 to 30	Typical parameters required of a water analysis in order to assess its corrosivity and probability of zinc corrosive properties.		
Calcium Hardness (as CaCO ₃)	mg/l	30 to 100			
Total Hardness (as CaCO ₃)	mg/l	50 to 150			
Total Dissolved Solids	mg/l	50 to 150			
Conductivity	µMs	>200			

Temperature and Pressure

Chemical reactions are generally accelerated by a rise in temperature; roughly, the rate of a reaction is doubled by a temperature rise of 10°C. This applies to corrosion of zinc by water, but there may be other temperature dependent reactions which offset the rate of corrosion, such as the precipitation of carbonates by displacement of the chalk-carbonic acid equilibrium, i.e. reduction in the dissolved oxygen content.

Hot dip galvanized piping is used for hot water supplies provided that the temperature does not exceed 65°C. At higher temperatures, the zinc will become electro-positive and hence cathodic to carbon steel. It is recommended that caution be exercised where hot dip galvanized systems are used above 65°C. Alternative or additional protective measures (Duplex) coatings need to be considered.

Water pressure per se is not a major factor in corrosion of zinc. However, it can have an indirect influence, such as increasing the oxygen retained in the water at low temperatures. Also note the effect of temperature, in combination with scale forming characteristics, discussed later in this paper.

Influence of pH levels (Refer to figure 2)

Zinc is an amphoteric metal, which means that it is soluble in acid (low pH) and also in high alkali (high pH) waters. The pH of water is of major importance as < 5.5 the rate of corrosion increases sharply unless inhibitors are present. Fundamentally however, the speed of corrosion is dependent upon the type, quality and mode of precipitation of corrosion products, with the most important zinc “product of corrosion” being zinc carbonate (ZnCO₃). The formation of a tightly adhering stable “Barrier Protective” zinc carbonate (ZnCO₃) film is required for the effective corrosion protection of carbon steel using any form of zinc coating. The zinc corrosion products in acids (pH<5.5) are readily soluble in water. In strongly alkaline solutions (pH>12.5) water-soluble zincates are formed. The suitability of hot dip galvanized coatings requires a pH range of >5.5 and <12.5. Time of wetness, agitation, suspended solids, hard or soft water and temperature all affect the formation of the ZnCO₃ protective patina.

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Zinc requires exposure to the environment for the formation of the $ZnCO_3$ barrier protective film. Stagnation can be unfavourable, while too much agitation may also erode the protective film. This action may be further assisted through erosion by suspended solids. At low temperatures, compact, adherent protective deposits are formed, which at higher temperature may become porous and non-protective.

Scale Forming Water

Hard waters are scale forming, whereas the degree of softness of water reduces the scale-forming characteristics. Scale forming tendencies of water are governed by the relationship between the amounts of calcium (Ca), Magnesium (Mg), Sulphates (SO_3), Carbonates (CO_4^{--}), Bi-Carbonates, Carbon Dioxide (CO_2), temperatures, and total dissolved solids (TDS) in the water.

In general terms, galvanized steel is best suited to hard waters. Galvanized steel is prone to attack in soft waters containing less than 50mg/litre calcium carbonate ($CaCO_3$).

With scale-forming waters zinc has an extended life where the determining factor with pipes can often be the gradual reduction in the effective internal diameter due to the scaling phenomena resulting in excessive scale deposits. Hot dip galvanized steel with zinc coatings typically 60 -100 μm thick, are widely used for pipes, water cylinders, tanks and handling domestic water systems with satisfactory results.

A number of indices have been used to define the scale forming tendencies of water. The most commonly encountered is the **Langelier Index (LI)**. A Langelier Index >2 shows a highly scaling water, whereas <0 (zero) indicates a non-scaling water. The indices are to be used as a guide, together with the other pertinent information that should be considered. Table No.3 is included for calculating this index, including a worked example.

Hot Water Systems

In hot water, the story is different. Scale forms on the zinc surface at water temperatures above $55^\circ C$ (Thomas, 1980); the scale that forms will have a coarse-grained structure with low adhesion to the zinc surface. Corrosion of the zinc will occur locally due to discontinuities in the scale and from local electrochemical action. When the local attack develops sufficiently to form a pit that exposes the steel, attack will favour the steel rather than on the zinc. This later process is due to a reversal of electrochemical polarity whereby the steel becomes anodic to the zinc. With most tap waters this reversal occurs at approximately $65^\circ C$ and it is good practice to 'run in' a new water system below $55^\circ C$ for the first year, both for the aforementioned reason and also to enable a thicker deposit to be formed.

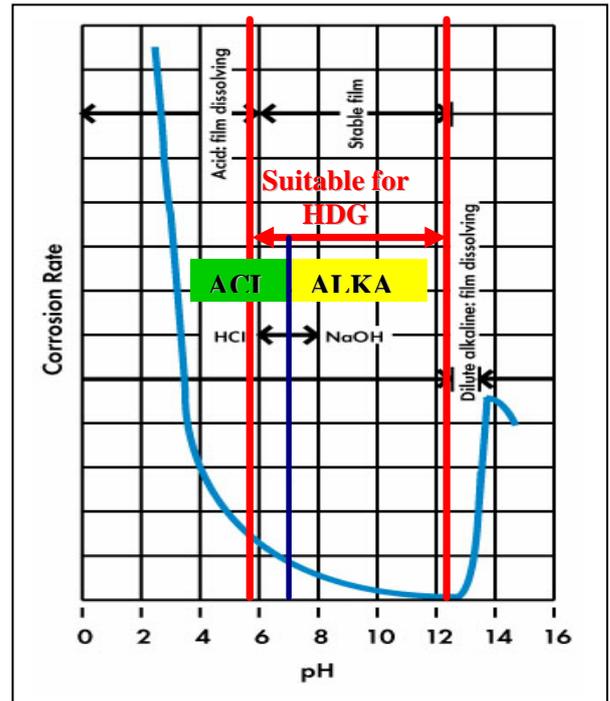


Figure 2: The reaction of pure zinc in a varying pH environment

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Microbial Influenced Corrosion (MIC)

This form of corrosion attack is caused by the presence of micro-organisms or bacteria. While not harmful from a health perspective, bacteria can result in severe attack of steel, zinc and other metals.

Anaerobic bacteria are frequently encountered in stagnant waters where oxygen levels become depleted. As the name implies, these bacteria are unable to survive in an oxygen rich environment. The organism absorbs sulphates present in the water or soil, which excrete substances containing sulphuric acid. Such acid cause localised pitting corrosion at sites on the metal surface where the bacteria forms a colony beneath a hard blackish brown protective nodule. Anaerobic conditions cannot generally develop in flowing distribution water systems where adequate chlorination is correctly applied.

In the event that the distribution is poorly chlorinated, allowed to stagnate for any extended length of time or intermittently operates, MIC may initiate. Recommencing of the operation does not necessarily eliminate the attack, due to the fact that the bacteria sites may have had sufficient time to form a hard protective crust or nodule under which the colony continues to survive and flourish.

Aerobic (oxidising) bacteria can also cause severe localised corrosion attack in oxygen rich environments such as on continually moist metal surfaces exposed to the atmosphere.

The Influence of Nitrates and Ammonia

Nitrates can also promote corrosion. However, when combined with ammonia compounds aggressive conditions may arise due to the development of high levels of alkalinity. Ammonia compounds should be limited to <50mg/l as they may form soluble zinc compounds, which will accelerate the removal of the protective zinc coating.

Effects of Copper

Hot dip galvanized piping is attacked in the presence of dissolved copper (Cu^+) within a common plumbing system (Cu is electro-positive to Zn). However, in practice, provided that the water is hard, these problems are rare. The preferred practice is to connect copper ancillaries downstream from hot dip galvanized pipes and fittings. Where copper, brass or bronze are in electrical contact with zinc and in the presence of an electrolyte (water), the zinc being electro-negative, will "sacrifice" itself to protect these metals. Refer to the galvanic series of metals illustrated with figure 3.

Corrosivity Index

As an additional indication of the corrosion characteristics of hot dip galvanizing, the Corrosivity Index (CI) formula may be used as a guide.

$$\text{CI} = \frac{[\text{Cl}^-] \times 0.03 + [\text{SO}_4^{2-}] \times 0.02}{[\text{HCO}_3^-] \times 0.02}$$

Where
[Cl⁻] = concentration of chlorides, mg/l
[SO₄²⁻] = concentration of sulphates, mg/l
[HCO₃⁻] = total alkalinity, mg/l (as CaCO₃)

Hot dip galvanized coating may be considered suitable if the CI < 1.

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Probability of Corrosion Occurring

The information contained in DIN 50929 Part 3 was used to compile the following guide to the "Probability of Corrosion". The information derived from this calculation should be used in combination with the other guidelines detailed in this paper.

The probable performance of hot dip galvanizing is derived using Table No.2 and applying it to the formula and comparing the results with the criteria indicated below.

$$\text{Probability of Corrosion (P)} = A+B+C+D+E$$

Where $P > 1$ corrosion control using zinc (hot dip galvanizing) is satisfactory.
 $P = 1$ to -3 corrosion control is fair
 $P < -3$ performance is unsatisfactory

Table No.2 Additional Parameters for Probability of Zinc Corrosion

Value	Parameter	Unit	Rating
A	Type of Water		
	Flowing		-2
	Standing		+1
	Anaerobic		-5
B	[Cl] x 0.03 + [SO₄²⁻] x 0.04	mg/l	
	<5		0
	5-25		-1
	>25-100		-2
	>100-300		-3
	>300		-4
C	Total Alkalinity	mg/l (as CaCO ₃)	
	<50		-1
	51-200		1
	201-300		0
	>301		-1
D	Calcium Hardness	mg/l (as CaCO ₃)	
	<50		0
	50-200		2
	201-800		3
	>801		4
E	PH		
	<5.5		-6
	5.5-6.5		-4
	6.5-7.0		-1
	>7.0		1

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Table No.3 Data for calculation of Langelier Index

Calculation of the Langelier Index							
Total Dissolved Solids		Temperature		Calcium Hardness		Alkalinity (pH 4.5)	
mg / l	A	° C	B	mg / l as CaCO ₃	C	mg / l as CaCO ₃	D
50-100	0.1	0-1	2.6	10-11	0.6	10-11	1.0
400-4000	0.2	2-6	2.5	12-13	0.7	12-13	1.1
> 4000	0.3	7-9	2.4	14-17	0.8	14-17	1.2
		10-13	2.3	18-22	0.9	18-22	1.3
		14-17	2.2	23-27	1.0	23-27	1.4
		18-21	2.1	28-34	1.1	28-35	1.5
		22-27	2.0	35-43	1.2	36-44	1.6
		28-31	1.9	44-55	1.3	45-55	1.7
		32-37	1.8	56-69	1.4	56-69	1.8
		38-43	1.7	70-87	1.5	70-88	1.9
		44-49	1.6	88-110	1.6	89-110	2.0
		50-56	1.5	111-138	1.7	111-139	2.1
		57-65	1.4	139-174	1.8	140-176	2.2
				175-229	1.9	177-220	2.3
				230-279	2.0	221-279	2.4
				280-349	2.1	280-359	2.5
				350-439	2.2	360-449	2.6
				440-559	2.3	450-559	2.7
				560-699	2.4	560-699	2.8
				700-879	2.5	700-899	2.9
				880-1049	2.6	890-1109	3.0
				1050 - 1409	2.7	1110-1399	3.1
				1410-1759	2.8	1400-1769	3.2
				1760-2220	2.9	1770-2239	3.3
						2240-2819	3.4
						2820-3159	3.5
						3160-3549	3.6
						3550-4459	3.7
						4460-5600	3.8

1. Obtain values of A, B, C and D from above table.
2. $pH_s = (9.3+A+B) - (C+ D)$
3. Langelier Index = pH – pH_s

For example: TDS 400 mg/l = 0.2 (column A)
 Temperature 25° C = 2.0 (column B)
 Calcium Hardness 240 mg/l = 2.0 (column C)
 Alkalinity 196 mg/l = 2.3 (column D)

Substituting into 2: $pH_s = (9.3+0.2+2.0) - (2.0+2.3) = 7.2$
 At pH = 7.2 LI = pH – pH_s = 7.2-7.2
 LI = 0

For hot dip galvanized coatings LI > 2.

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Conclusion

From the above discussion, it should be evident that determining the corrosion control performance of hot dip galvanized coatings in water is not an exact science, and is dependent on a number of synergistic and inter-related factors. Some of the major factors have been addressed in order to provide guidance as to how zinc, in the form of hot dip galvanizing, will react when used with varying water compositions.

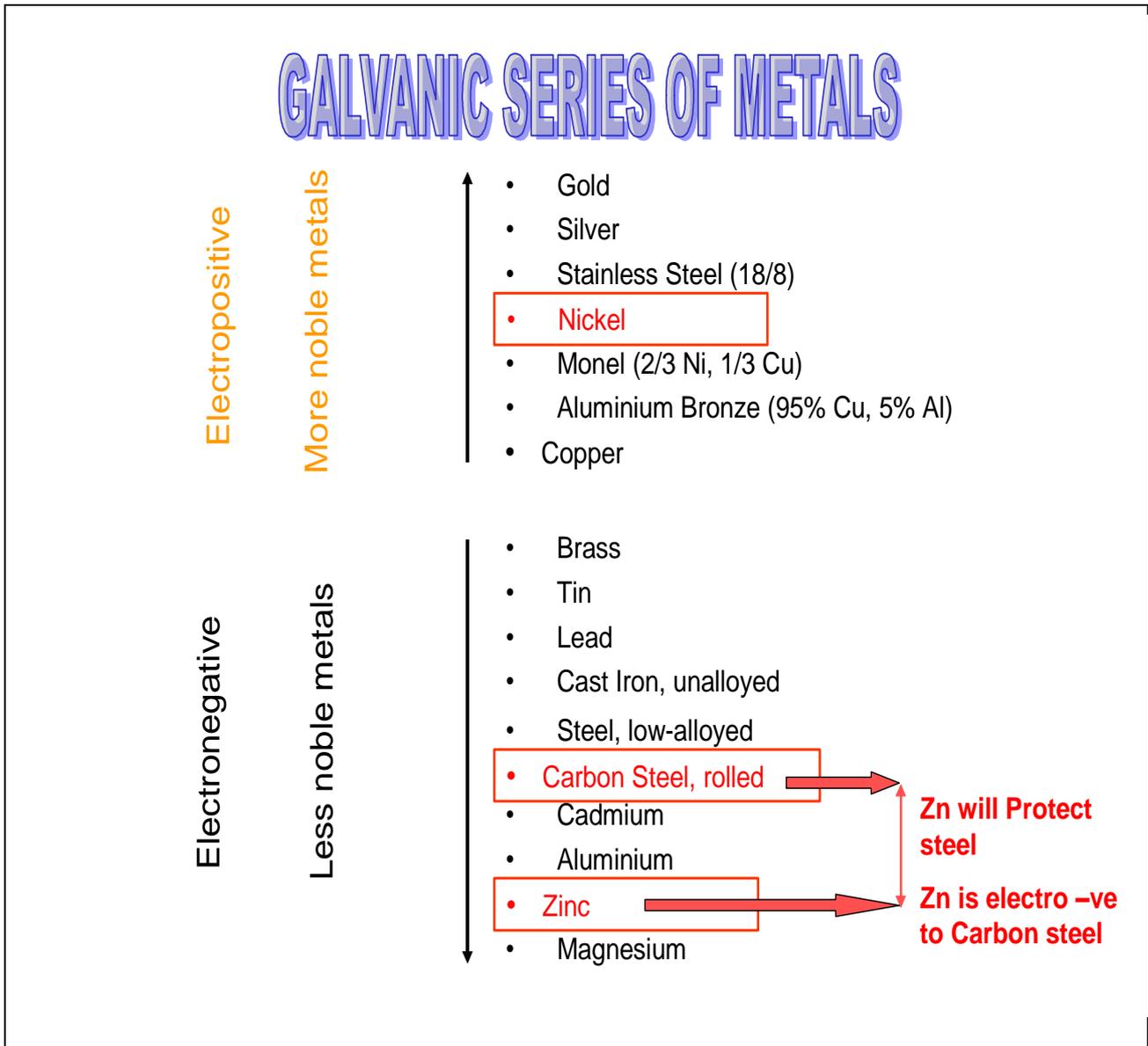


Figure 3: An example of the Galvanic Series of metals immersed in sea water. Refer to Information Sheet No.11 “How Does Zinc Protect”

For additional information on the subject matter refer to; Information Sheet No.3 “Corrosion of Hot Dip Galvanized Steel (Zinc) in Water” and Information Sheet No.11 “How Does Zinc Protect?”