

Armorgalv Thermal Diffusion Coating
Factors in In-Ground Performance Report
For
Armorgalv (Aust) Pty Ltd.

John Robinson
Director
Mount Townsend Solutions Pty Ltd

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ArmorGalv Coated Steel In-Ground

INTRODUCTION

There are many applications where steel is used in the ground, from simple applications like sign posts and fence posts, to engineered applications like piling and foundations, while the mining industry uses large quantities of steel for its strata control products.

It is not practical to install expensive corrosion management technologies on many of these embedded steel products, as is the case for more critical infrastructure such as pipelines and tunnels. An understanding of the mechanism of corrosion will allow a predictable life to be designed into critical steel construction products and facilitates the selection of protective coating systems that offer the best cost/performance solution to the product's longevity.

STEEL CORROSION IN-GROUND

In the atmosphere, most materials have predictable modes of corrosion that are largely dependent on pollution levels, temperature and relative humidity. Once the important parameters are identified, the mechanism of metallic corrosion will then be common to all the products that are within that climatic zone.

In-ground situations are vastly different because of the wide local variations in soil chemistry, moisture content and conductivity that will affect the way coated or uncoated steel will perform in the ground.

Research into steel corrosion in soil started in the early years of this century, when Melvin Romanoff began a study for the National Bureau of Standards that continued for over 40 years. Many other corrosion-in-soil research projects were undertaken concurrently or subsequently. Much of this activity has taken place in Australia sponsored by various road authorities and private enterprise companies such as BlueScope Steel and Ingal Civil Products, in evaluating in-ground corrosion performance on a range of products from culverts to piling.

Corrosion of metals in soil is extremely variable and while the soil environment is a complex one, it is possible to draw some conclusions about soil types and corrosion.

Any given soil will appear as a very heterogeneous electrolyte which consists of three phases:

- The solid phase made up of the soil particles which will vary in size and will vary in chemical composition and level of entrained organic matter.
- The aqueous phase which is the soil moisture - the vehicle which will allow corrosion to take place.
- The gaseous phase which consists of air contained in the soil's pores. Some of this air may dissolve in the aqueous phase.

THE SOLID PHASE

Soils are commonly classified according to the general size range of their particulate component. Sandy, silty and clay soils are thus identified from the predominant size range of their inorganic particles. Convention classifies particles over 0.07mm to around 2mm as sands, particles from 0.005mm to 0.07mm as silts and 0.005mm smaller as clays. Soils rarely exist with only one of these components present.

The various groups of sand, silt and clay make up the soil classifications on the basis of their particle size.

Clay soils are characterised by their ability to absorb water readily, the level of which is determined by the nature of the clay. For this reason, clay soils present a significantly higher corrosion risk than sandy soils. For this reason also, the nature of the soil on the surface may not reflect its nature below the ground.

THE AQUEOUS PHASE

Corrosion will only occur in the presence of moisture that contains ions that will transmit the electric current maintaining corrosion activity. There are several types of soil moisture. These are:

- free ground water
- gravitational water
- capillary water.

The free ground water is determined by the water table, which may range from near ground level to many metres below the surface. This is the least important factor in determining corrosion of buried steel as most installations are above normal water tables. Where high water tables bring ground water in contact with embedded steel, corrosion will progress as if the steel were in an immersed environment.

Gravitational water arises from rainfall or man-made irrigation and will soak into the soil at a rate determined by its permeability. This will increase the period of wetness of the steel's surface and this in turn will impact on the soil's corrosive effects, depending on the conductivity of the gravitational water. Where regular rainfall occurs, most soluble salts may be leached from the soil over time, which will reduce the corrosive effects of gravitational water. Gravitational water will ultimately end up in the water table.

Capillary water is water that is entrained in the pores and on the surfaces of the soil particles. The ability of soil to retain moisture is obviously important to plant growth. It is the capillary water that is the prime source of moisture in determining corrosion rates of steel in soil.

The fluctuations in water content in soil due to precipitation and evaporation cause a variation in oxygen content, as drier soils allow more oxygen access and oxygen concentration cell formation may be enhanced.

SOIL CHEMISTRY

Acid or alkaline conditions develop in the soils depending in their parent rock and the geological or man-made activity that may impact on them over time. Most soils are in the pH range of pH 5.0 to pH 8.0. Highly acidic soils are relatively rare, and generally occur in swamp soils or areas subjected to high accumulations of acidic plant material such as pine needles.

Soluble salts are essential to plant growth and are a major factor in corrosion. These salts may include salts of potassium, sodium, calcium and magnesium. Salts such as calcium and magnesium, while initially promoting corrosion, frequently act beneficially as their insoluble oxides and carbonates become corrosion inhibitors over time.

Bacteria in soil is another factor that is important in corrosion activity. Sulfates can promote rapid bacteriological corrosion of steel because of sulphate reducing bacteria. Hydrocarbon-using bacteria can accelerate failure of organic coatings used underground also.

Soil has to be able to conduct electricity to participate in the corrosion of buried steel. The resistivity of the soil is used as an important measure of soil corrosivity. The higher the resistivity,

the more the resistance to current flow moving between anodic and cathodic regions of the steel.

Regions of moderate or high rainfall will commonly have low levels of soluble salts in the soil, while desert soils may have very high salt levels. Some of the most aggressive soils in Australia are located in desert areas like the Simpson Desert clay pans have higher corrosion rates for steel and zinc coatings than many surf-side environments.

IN-GROUND CONDITIONS IN THE MINING INDUSTRY

While much in-ground research has been focused on ground-line installations, the soil conditions in underground mining applications are likely to be quite different. In mining applications, the main factors affecting the interaction between steel strata control products are the morphology of the rock in contact and the presence or otherwise of ground water its pH and its constituents.

In underground mining environments, it is likely that some of the factors influencing corrosion rates of steel arising from high levels of organic matter, aeration and precipitation will not be present.

However, the basic principles of assessment for in-ground corrosivity can still be applied, particularly with respect to resistivity and pH.

ESTIMATING SOIL CORROSIVITY

A great deal of case history data and specific research has been accumulated and this is invaluable in evaluating the potential for corrosion for various types of buried structures. While there are no easy answers, the German Gas and Water Works Engineers Association has developed a standard soil corrosivity assessment technique which rates the various factors that influence corrosion of steel in the ground detrimentally or beneficially. The sum of these factors gives an approximate corrosion rating.

TABLE 1

SOIL CORROSIVITY ASSESSMENT TECHNIQUE

Item	Measured value	Mark
Soil composition	Calcareous, marly limestone,	+2
	sandy marl, not stratified sand.	
	Loam, sandy loam (loam content	0
	755 or less), marly loam sandy	
	clay soil (silt content 75% or less)	
Ground water	Clay, marly clay, humus	-2
	Peat, thick loam, marshy soil	-4
	None	0
Resistivity	Exist	-1
	Vary	-2
	10,000 ohm.cm or more	0
	10,000 - 5,000	-1
	5,000 - 2,300	-2
Moisture content	2,300 - 1,000	-3
	1,000 or less	-4
	20% or less	0
pH	20% or more	-1
	6 or more	0
Sulphide and hydrogen sulphide	6 or less	-2
	None	0
	Trace	-2

	Exist		-4
Carbonate	5% or more		+2
	5-1%		+1
	1% or less		0
Chloride	100 mg/kg or less	0	
	100 mg/kg or more	+1	
Sulphate	200 mg/kg or less		0
	200 -500 mg/kg		-1
	500 - 1000 mg/kg		-2
	1000 mg/kg or more		-3
Cinder and coke	None		0
	Exist		-4
Soil rating:	0 or above - Non-corrosive		
	0 to -4 - Slightly corrosive		
	-5 to -10 - Corrosive		
	-10 or less - Highly corrosive		

CORROSION CASE HISTORIES

While corrosion rates can be estimated using theoretical assessment, the one certainty is that in real life, the unexpected will always happen. For this reason, case history studies are very important for establishing performance benchmarks. Interest in the corrosion of steel buried structures has always been maintained, and a constant stream of information from a wide variety of sources is available.

There are two issues that determine the life of buried steel. The first is the life of the protective coating and the second is the corrosion rate of the steel. The item can be deemed to have failed when the steel loss is sufficient to prevent the steel performing its structural function.

Where polymer coatings are applied to buried steel items, most commonly pipelines, the failures are rarely caused by general deterioration of the coating. Localised failure due to holidays in the coating or pin holing or large-scale corrosion related to electrolysis are common causes of failure in these installations.

Metallic coatings, specifically zinc-based coatings, fail through progressive consumption of the coating by oxidation or chemical degradation. The rate of degradation is approximately linear, and with zinc coatings of known thickness, the life of the coating then becomes a function of the coating thickness and the corrosion rate. It should be noted that zinc-based coatings applied to a range of steel products can differ significantly in their metallurgical characteristics, and these differences can have a major effect on the rate at which the coating corrodes.

Steel corrosion can be assessed similarly, although the body of case history evidence indicates that corrosion rates of steel in soil decrease with time as corrosion products block access of the corrodants to the steel surface. Studies of steel piling corrosion in the USA in severe environments have shown initial corrosion rates exceeding 100 microns per year in the first two years of service, falling to an average of 50 microns per year over the first 20 years to stabilise at 25 microns per year after that.

BlueScope Steel has done extensive testing of its steel piles over a number of years and has drawn the following conclusions based on case history measurements of piles in Victoria:

Corrosion rate of steel in undisturbed soil/compacted fill	10-20 microns per year
Corrosion rates of steel in fill sites - low compaction	20-30 microns per year

Corrosion rates of steel in fill sites subject to tidal movement

30-50 microns per year.

CORROSION RATES AND AUSTRALIAN STANDARDS

The use of corrugated steel culverts has been long established in Australia. A standard has been developed and the most recent revision, AS/NZS 2041:1998, contains a significant amount of useful information in its Appendix C on durability issues.

There are a number of informative tables in this Standard that address corrosion issues for a variety of coatings as well as the base steel. These tables base corrosion rates on soil resistivity and pH as well as soil classifications. These tables nominate corrosion rates for galvanized coating from around 3 microns per year in well drained soils with neutral pH to over 20 microns per year in undrained acidic (pH<4) soils.

Metal loss for steel is nominated at less than 10 microns per year in well-drained soils with high resistivity and pH greater than pH5, to 300 microns per year in poorly drained soils with low resistivity (usually related to chloride concentration). Reasonable averages derived from these tables for both zinc and steel in contact with soil are for zinc, 6-10 microns per year, and for steel, 20-30 microns per year. In in-ground conditions where there is no moisture present, corrosion is likely to be negligible.

DETERMINATION OF PRODUCT LIFE IN-GROUND

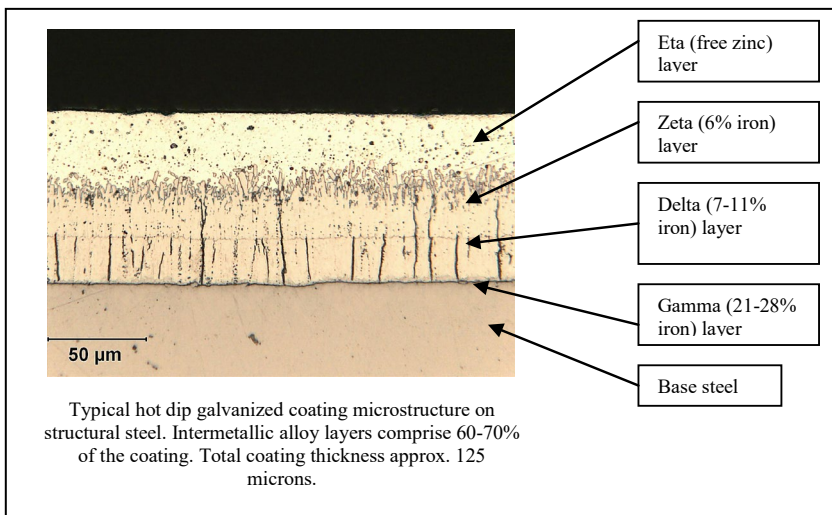
HOT DIP GALVANIZED COATINGS

Given that the steel used in strata control and related underground mining operations is designed for its specific engineering purpose, and does not have what can be considered extra steel to accommodate a corrosion allowance, the performance of the protective coating becomes the most significant factor in determining the durability of the component.

Because of the highly abrasive conditions involved in underground mining operations, applied paint coatings are rarely considered, and traditionally, hot dip galvanized coatings have been specified for a large proportion of the strata control products used in the industry.

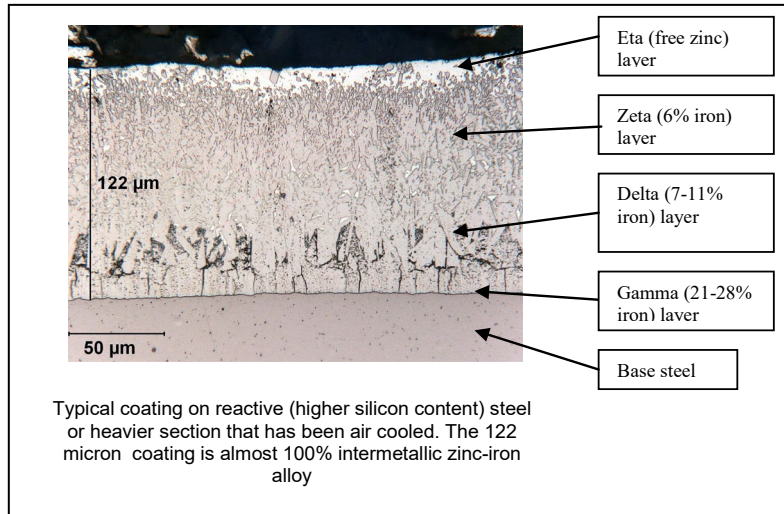
The reason that hot dip galvanized (HDG) coating have good abrasion resistance, is that unlike many other zinc-based protective coating (continuously galvanized sheet, wire and tube and electroplating) the majority of the HDG coating is not relatively soft zinc, but a zinc-iron alloy formed through the reaction of the steel with the molten zinc. A typical HDG coating on steel of standard chemistry is shown in Figure 1.

Figure 1.



Reactive steel will generate thicker zinc-iron alloy layers as is illustrated in Figure 2. This variation in coating characteristics is generally beyond the control, of the galvanizer and is determined by steel chemistry, surface condition and section thickness (this determined immersion time in the molten zinc)

Figure 2



It should be noted that while the percentage of zinc in these zinc-iron alloys is relatively high – 92-95% depending on the proximity to the steel's surface - this part of the HDG coating is significantly different to pure zinc coatings in its mechanical properties and its corrosion resistance characteristics.

The disadvantage of HDG coatings on some products arises because the HDG process is an immersion process and on withdrawal from the molten zinc batch, the surface tension of the zinc and the fact that the galvanizing temperature (455 °C) is only slightly above the solidification temperature of zinc (420 °C) results on drainage issues, particularly on threaded products, products with blind holes and products requiring clearances for moving parts.

Most externally threaded items that are hot dip galvanized require processing in special centrifuge facilities for small parts, or post-galvanizing treatment of the threads by reheating and wire brushing at additional cost.

Two particular limitation of the HDG process on specific products and materials are:

1. Internally threaded items – specifically structural nuts- cannot be hot dip galvanized internally because of zinc entrapment in the internal threads. It has thus been industry practice to have the nut blanks galvanized and cut the internal threads after galvanizing. This means that all hot dip galvanized nuts have no protective coating on the internal threads, and rely on the intimate contact with the external threads on the bolt for their corrosion resistance.
2. Steels grades exceeding 800 MPa in strength are susceptible to hydrogen embrittlement in the HDG process through exposure to the pickling acids used in the process. This limits the use of HDG in many structural bolting applications, including foundation bolts

and tension members used in post-tensioned concrete structures.

THERMAL DIFFUSION COATINGS

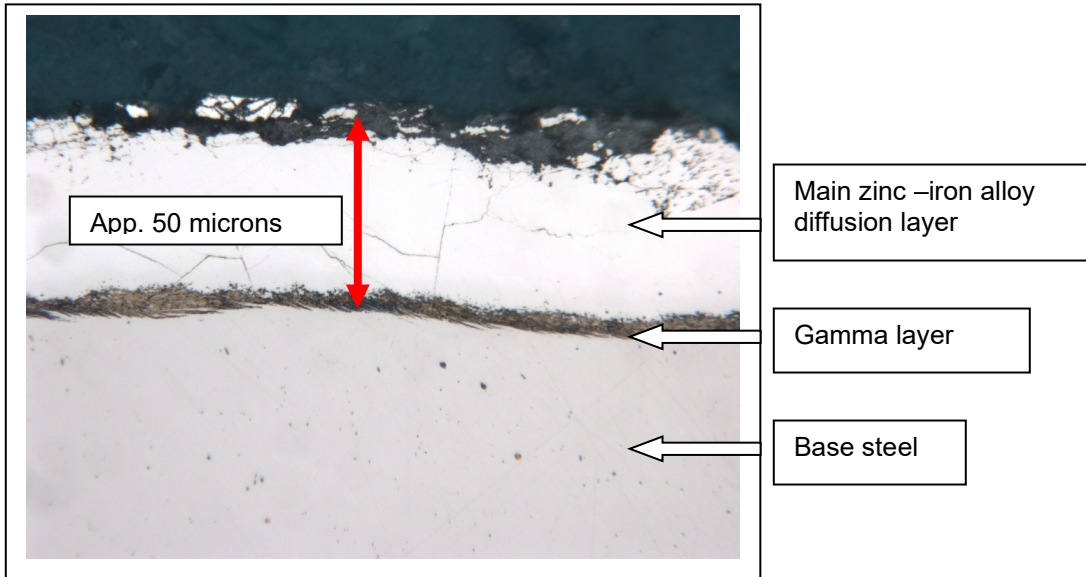
Thermal diffusion coatings are not unlike the alloy layers formed in the galvanizing process, but have several significant differences in their application. They are not new, having initially been developed by Englishman Sherard Cowper-Coles in 1900. He gave his name to the process commonly called sheradising. For much of the 20th Century, sheradising was confined to the thermal diffusion coating of small parts – particularly fasteners.

The unique feature of the this thermal diffusion process is that the zinc-iron alloy is formed on the steel’s surface at temperatures below the melting point of zinc – in other words, it is a solid state reaction. The process and the coatings characteristics in comparison with other metallic zinc-coating processes will be covered in more detail in a subsequent document.

Because the steel items to be coated are in intimate contact with the specially activated zinc powder that is used in the process, and are usually rotated in a heated kiln facility, all surfaces, including internal threaded surfaces are uniformly coated with the thermal diffusion coating, whose thickness is closely controlled by the process control systems.

While the thermal diffusion coating is similar to a reactive HDG coating, its proportion of zinc to steel in the alloy formed tends to be more uniform in the outer layers of the coating, and of higher steel content in the thin gamma layer adjacent to the steel’s surface.

This is illustrated in the micrograph (Figure 3) of the typical thermal diffusion coating applied by Armorgalv to a steel component of normal chemistry.



The beneficial characteristics of this type of coating include its uniformity on all surfaces, its enhanced anti-corrosion properties because the coating has no free zinc exposed on its surface, its hardness (abrasion resistance) and its anti-galling properties, once again as a result of there being no free zinc on the surface of the coating.

DURABILITY OF THERMAL DIFFUSION COATINGS

There is a body of evidence that supports the fact that thermal diffusion coatings as applied by ArmorGalv have superior corrosion resistance to plain zinc-based coatings. Exposure testing by CSIRO at its marine exposure site at Point fairy in Victoria, and other laboratory-based accelerated weathering testing done by the thermal diffusion coating industry had indicated that the corrosion rate of zinc-iron alloys is typically 2-3 times lower than that of pure zinc.

The deterioration or weathering of a zinc coating is an oxidation process that consumes the zinc at a rate that is determined by the environment to which it is exposed. The process is as follows:

1. The oxidation reaction $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$
2. The hydration reaction $2\text{Zn} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Zn}(\text{OH})_2$
3. Carbonation $5\text{Zn}(\text{OH})_2 + 2\text{CO}_2 \rightarrow 2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2 + \text{H}_2\text{O}$

The zinc requires the carbonation process to form the stable oxide film on its surface to limit the rate of oxidation over time. Interference with the formation of this carbonate oxidation layer through exposure to chlorides, sulfates or pH solutions outside the pH6-8 range can compromise the durability of the zinc coating.

An additional standard component of the ArmorGalv process is an immersion passivation stage following the application of the thermal diffusion coating. This performs an accelerated carbonation function that significantly reduces the surface oxidation of the coating in its early life – a factor that results in the coating loss in the first 12 months of a hot dip galvanized coatings life in normal atmospheric exposure, being 3-5 times higher than that achieved when its passivation films are stabilised over time.

Zinc is an amphoteric metal and will react with both acids and alkalis. Iron performs poorly in acidic exposures but has excellent performance in alkaline environments. The zinc-iron alloy in a thermal diffusion coating thus has quite different and superior corrosion resistance characteristics than standard zinc coatings.

SUMMARY

Thermal diffusion coatings are particularly well suited to applications in the underground mining industry, and solve a number of problems related to the use of hot dip galvanized coatings on strata control products.

The limitations of traditional thermal diffusion coating processes has been their inability to process anything other than small components. The development of the ArmorGalv process in Australia has allowed much larger products (up to 3.2 m long) to be thermal diffusion coated successfully at an economical cost and offer a highly durable solution to corrosion management in the underground mining industry.

In addition, the ArmorGalv process has a high environmental rating, as there are no chemical residues, fumes or solid waste products arising from the process

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