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## Specifications for corrosion protection in the copper mining industry in Chile

Christian Sánchez Villa<sup>a</sup>

### Abstract

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The technical specifications for the protection of steel structures for copper mining in Chile, should respond to the high durability requirements avoiding most of the maintenance activities. To meet this challenge, protection systems have had to evolve and solutions that meet these requirements have had to be developed. International experience suggests that through a proper analysis of project requirements, including corrosive environments, a correct specification is a key question. The emphasis is on the classification of atmospheric corrosion in mining processes ranging from mining to shipping at the port. At this stage, it is essential to consider tools that are able to assess the cost of coating throughout their service life cycle, considering the initial investment costs, corrosive atmosphere and time to first maintenance, among other variables. Protection systems based on duplex coatings have shown great versatility, responding to the demands of the mining industry, where the cost of process shutdown is very high and the accident prevention becomes essential. This type of coating drives the performance of galvanized and paint schemes, taking advantage of their synergistic features.

**Keywords:** corrosion, duplex system, copper mining, protective coating.

### Introduction

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The selection of an adequate protection system is based on the service life requirements of the structure without maintenance. Undoubtedly this is associated to the environmental conditions to which the structures are exposed.

The influence of weather parameters such as environmental humidity, rain, wind speed and direction; geographical parameters, mainly proximity to coastal areas and industrial activities in the surroundings are fundamental to determine the corrosiveness of a particular environment.

Tools have been developed to classify corrosive environments; one of them is the atmospheric corrosiveness classification provided by ISO 9223 (1) where it indicates that the resistance to atmospheric corrosion of the different materials depends on weather factors such as environmental humidity, precipitations, proximity to the coast and very importantly, the presence of contaminants, because depending on the type and amount of contaminants present, there will be behaviour variations in face of corrosion.

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<sup>a</sup> Master, Civil Engineer – BBosch Recubrimientos, Chile

The corrosion protection recommendations given in ISO 12944 (2) and ISO 14713 (3), in first place, consider what is mentioned in ISO 9223 and classify corrosive environments in six categories. They also give examples of each one of them together with the minimum and maximum corrosion rates for bare steel and zinc in each case, as summarized in Table 1.

**Table 1** - Corrosivity classification as in standard ISO 12944-2

Corrosivity category	Exterior	Interior	Annual thickness loss, $\mu\text{m}$	
			Steel	Zinc
<b>C1</b> very low	-	Heated buildings with clean atmospheres, e.g. offices, shops, schools, hotels.	$\leq 1,3$	$\leq 0,1$
<b>C2</b> low	Atmospheres with low levels of contamination. Rural areas mostly.	Unheated buildings where condensation can occur, for example: sports centers stores.	$>1,3 - 25$	$>0,1 - 0,7$
<b>C3</b> medium	Urban and industrial atmospheres with moderate sulfur dioxide pollution. Coastal areas with low salinity.	Manufacturing buildings with high humidity and some air pollution, for example, food processing plants, laundries, breweries, dairy plants.	$>25 - 50$	$>0,7 - 2,1$
<b>C4</b> high	Industrial areas and coastal areas with moderate salinity	Chemical plants, swimming pools, coastal vessels and shipyards.	$>50 - 80$	$>2,1 - 4,2$
<b>C5I</b> Very high industrial	Industrial areas with high humidity and aggressive atmosphere	Buildings or areas with almost permanent condensation and high contamination levels.	$>80 - 200$	$>4,2 - 8,4$
<b>C5M</b> Very high marine	High salinity coastal and marine areas	Buildings or areas with almost permanent condensation and high contamination levels.	$>80 - 200$	$>4,2 - 8,4$

### Duplex systems protection

The so-called duplex systems consist on the steel protection with a paint scheme applied on a zinc coating. The purpose is to expand the zinc coating utilization toward applications that require a better behaviour in face of corrosion when they are exposed to environments where the galvanizing by itself doesn't provide the durability required for the protection of the project, taking advantages of the synergistic characteristics between the distinctive coatings and the paints.

Hot dip galvanizing is a protection procedure for corrosion of materials and items manufactured with iron and steel. It consists on the dipping of those materials and items in a melted zinc dip. In this manner, on top of these materials, protective zinc and zinc-iron alloy coatings are formed, and they are perfectly adhered to the base substrate through metallurgical bonding.

“Duplex Systems” is a term adopted by J.F.H. Van Eijnsbergen (4), Dutch corrosion expert, in early 50s. The term describes the steel protection through a zinc coating that in turn is

covered by a non-metal coating. The purpose is to give additional strength against corrosion when required, or when it is necessary to achieve an attractive appearance.

The duplex systems based on one or several painted layers on top of the galvanized coatings are used generally in the cases when it is necessary to have a very efficient corrosion protection. The most frequent examples are found in applications that require protection in the coastal areas (5), buildings, urban real state, road infrastructure and the chemical and mining industries.

The duplex systems duration is normally much longer than the one that could be calculated by the summation of the foreseeable duration for each individual system separately (6). It can be said that a synergistic effect occurs, and that mathematically we could explain it through the next formula:

$DT = K(D_{zn} + D_p)$  , where:

DT = Total duration of the duplex system

Dzn = Duration of the galvanized coating

Dp = Paint duration

K = A constant

The synergistic effect can be quantified (K constant value) between 1.3 and 2.7, depending on the paint system and the environmental conditions to which the system is exposed. Typically, the life addition factor in a quite aggressive weather is of 1.8 to 2.0; in seawater it is from 1.3 to 1.6 and in a nonaggressive climate it is from 2.0 to 2.7 (4).

Another fundamental factor in the selection of a protection system is the associated cost, where it is necessary to consider the cost through the structure's life cycle and data from different durability paint schemes published (7, 8), with initial investment costs and the costs that derive from the protection's maintenance; either direct maintenance costs or also costs associated to the shutdown of a process and accident risks.

### **The copper mining process in Chile**

The mining activity in our country involves production processes or stages that generate high corrosive environments, such as the case of hydrometallurgical processes (LIX-SX-EW) in the presence of sulfuric acid. This happens in every stage where we have exposure to direct condensation chemical attack with high concentrations of sulfuric acid, like the interior of electrowinning plants or leached copper ore handling, where protection is performed using powerful paint schemes based on epoxy Novolac systems. Elsewhere, there is exposure to mist with lower concentrations of acid or sulfuric acid carryover from the leach pad by prevailing winds. The latter shows the criticality of protecting nearby structures such as electrical substations, which are typically protected with hot-dip galvanizing. The experience has shown that these structures need maintenance for their first time just after 16 years.

In less corrosive environments, such as areas of dry mineral processing, crushing, overland conveyors and stockpiles, for example, you can have a durability of more than 50 years without any maintenance. Wet zones, conventional and SAG grinding, flotation, filter plant

and port structures have favorable conditions for duplex systems protection (galvanizing plus paint).

Large copper deposits in Chile are mostly located in the Atacama Desert, in the north zone of the country. The mining and size reduction activities in primary crushing stages are made in zones near the deposit, the downstream stages are farther away and depend on the type of ore that is being processed; Copper sulfides and copper oxides.

### **Copper sulfides**

The copper sulfide ores are processed by grinding and concentration through froth flotation. Copper concentrates are obtained and then processed through pyrometallurgy to obtain fire-refined copper in ingots or anodes that are electrorefined to produce copper cathodes with 99.999% purity.

#### **Primary crushing stage and dry mineral handling**

Normally, this stage is located nearby the mining places, in some cases within the mine. This environment considers crushing stages, overland conveyor belts and dry ore stockpiles. Generally, these sectors show low corrosion rates and the corrosive aggressiveness condition mainly depends on the geographical environment.

That is how, if the dry area of a mining process is found in a desert climate, and as there is a condition of low humidity, the corrosion rate is very low and there are no galvanic components with the deposited mineral dust. In this case, the painting design required by these facilities is aesthetical more than anticorrosive.

Notwithstanding the above, the coatings must consider the situations of traffic exposure, UV radiation, abrasion and wearing out in stairs, handrails or others.

#### **Grinding and concentration**

The objective is the release of sulfide ore particles in order to separate them in froth flotation processes. In this stage, the size reduction is made in SAG mills and conventional mills. Water is added to the process to handle the ore as slurry, which means that there is a higher corrosiveness due to the increase in humidity and the contact of structures with the slurries.

Many mining sites conclude the process in this stage and the final product is transported to the ports through concentrate pipelines to be exported.

#### **Pyrometallurgical treatment**

The copper concentrate must be taken to pyrometallurgical processes where they are melted and refined through the oxidation of impurities and sulfur. One of the process outputs is sulfur dioxide, which is captured and taken to a sulfuric acid production plant. Approximately 1 % of the sulfur dioxide cannot be captured and escapes to the atmosphere, contributing to the corrosiveness in the surroundings.

The output from the pyrometallurgical plant is fire-refined copper with a 99.995 % purity in ingots or anodes that are electrorefined to form cathodes with 99.999% purity.

### **Copper oxides**

The ores that are made up by copper oxides are processed by hydrometallurgical means, through leaching-solvent extraction operations and by obtaining cathodes through electrowinning.

#### **Primary crushing stage and dry mineral handling**

As in sulfide minerals, the extraction and crushing stages are made with dry ore, the ore size is approximately 13 mm,

#### **Acidification and heap leaching**

The ore is taken to agglomerating drums where sulfuric acid is added and then it is taken to the leaching heaps through conveyor belts where it is irrigated with concentrated sulfuric acid solutions. The solution dissolves the ore and it is captured in the lower zones of the heap, resulting in a copper and iron pregnant solution (PLS).

#### **Solvent extraction (SX)**

The PLS solution is taken to solvent extraction, where it is put into contact with organic extractants that purify it.

#### **Electrowinning**

The purified solution enters into a copper electro winning circuit where cathodes are produced with 99.999 % of purity.

The wet areas present in hydrometallurgical processes involve sulfuric acid in different concentrations, resulting in the most aggressive environments in copper mining.

## **Results and discussion**

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### **Environmental classification**

The structures to be protected will be classified according to the aggressiveness of the environment to which they are subjected. According to this, the typical environments of the Plant are based on what is described in standards ISO 9223, ISO 12944-2 and ISO 14713.

#### **Dry Industrial Environment**

This is an environment similar to a C3 environment, intermediate corrosiveness, defined in ISO 12944-2, and it is present in environments with low humidity and contamination:

- Structures present in the Crushing Plant and Dry Ore Handling

- Upper structures in concentrator plants
- Project Area located outside of wet areas or areas susceptible to receive acid mist.

### **High corrosiveness industrial environment**

This environment is similar to a C4 environment defined in ISO 12944-2. It is seen in higher humidity and contamination environments, presence of SO<sub>2</sub> and structures located in areas with presence of vapors and acid mists with sulfuric acid content at concentrations not higher than 10 %. These areas correspond to the following facilities:

- Upper structures in filtering plants;
- Structures in thickeners;
- Reagent handling and storage area;
- Structures in lower levels of concentrator plants.

### **Very high corrosiveness industrial environment**

Environment similar to a C5 environment defined in ISO 12944-2, which is present in structures in areas that have vapors and acid mist with sulfuric acid content at concentrations not higher than 25%. These areas correspond to the following facilities:

- SX buildings;
- Zones outside the EW y SX bays;
- Zones near the leaching heaps;
- Structures at lower levels in the filtering plants;
- Interior structures in pyrometallurgical processes;
- Port infrastructure.

### **High aggressiveness industrial environment**

This is an environment of high aggressiveness, direct chemical attack of exposed structures in areas of vapors and acid mists with sulfuric acid content at concentrations higher than 70 %. These areas correspond to the following facilities:

- Acidifying drum zones and zones near and under acidified waste handling equipment (conveyor belts, chutes, etc.) susceptible of dripping and splashing of sulfuric acid;
- Handling zones, storage tanks and reception of sulfuric acid;
- Interior of the EW bay;
- SX-EW Tank yard.

### **Protection systems**

The classification of environments presented above is based on field observations and specifications of protection against corrosion in copper mining, where the protection specifications agree with industrial paints with the durability expected and actually obtained.

The paint systems must be selected qualitatively considering the following characteristics:

- They must be adequate for the specific need;
- There must be practical experience in the use under similar conditions;
- Expected life service or durability;
- To be available in the market at the desired color;
- To comply with local regulations.

For carbon steel structures protected by simple paint systems, the durability is considered up to 15 years.

The paint systems for the galvanized steel protection consider a high durability of more than 15 years.

The life service estimated for a paint system is defined as the time until the first paint maintenance or repair is made after 5 % to 10% of the substrate corrosion shows up (bare metal), or the equivalent to oxidation level 4 defined by the SSPC-VIS2 standard.

Four duplex systems and five traditional paint schemes are selected as an alternative to the duplex system or as a solution where the duplex systems don't have enough durability in extreme conditions environments with direct chemical attack.

Table 2, shows the protection systems according to the practical application and table 3 shows the system description.

**Table 2 - Corrosive condition and protection system**

Process area	Corrosive condition	Corrosive category ISO 12944-2	Protection system
Wet zone	Very high-high (acid presence)	Chemical attack according to ISO 12944-2 B.2.1	PS7
Leaching zone	Medium (diluted acid)	Chemical attack according to ISO 12944-2 B.2.1	PS7
Dry zone	Medium-low	C3	DS1/PS4
Concentrate zone	Medium-high	C4	DS2/PS5
Inside mine zone	Medium-high or high (depending on the type of water)	C4-C5I	DS2/DS3/PS4/PS5
Smelter and acid plant	High-very high (depending on sector)	C5I	DS3/PS5
Water tanks (interior)	High-very high	IM2	PS7
Ports	Very high (strong electrolyte)	C5M	DS4/PS5
Infraestructure	Low (depending on process)	C3	DS1/PS4
Rural	Low- medium (depending on process)	C3	DS1/PS4

Hot dip galvanizing is according to ASTM A123 standard.

The surface preparation of galvanized steel is according to ASTM D6386, and for bare steel according to SSPC SP10.

PS10 system is designed as reinforcement plates painted with polyester coating exposed to C5 corrosivity category.

**Table 3** - Protection system description.

System designation	Substrate	Primer coat	Intermediate coat	Top coat
DS1	Hot dip galvanizing cleaned as ASTM D6386	-	-	75 microns (dtf) Acrylic polyurethane
DS2	Hot dip galvanizing cleaned as ASTM D6386	50 microns (dtf) Polyamide epoxy	-	75 microns (dtf) Acrylic polyurethane
DS3	Hot dip galvanizing cleaned as ASTM D6386	50 microns (dtf) Polyamide epoxy	-	125 microns (dtf) Alliphatic aducto-amine epoxy
DS4	Hot dip galvanizing cleaned as ASTM D6386	50 microns (dtf) Polyamide epoxy	-	125 microns (dtf) Acrylic polyurethane
PS4	Bare steel, blast cleaned to near white metal	50 microns (dtf) Inorganic zinc	50 microns (dtf) Polyamide epoxy	75 microns (dtf) Acrylic polyurethane
PS5	Bare steel, blast cleaned to near white metal	50 microns (dtf) Inorganic zinc	50 microns (dtf) Polyamide epoxy	125 microns (dtf) Alliphatic aducto-amine epoxy
PS7	Bare steel, blast cleaned to near white metal	250 microns (dtf) Epoxy novolac	-	350 microns (dtf) Epoxy novolac
PS10	plates painted with polyester coating.	25 microns (dtf) epoxy isocyanate	100 microns (dtf) epoxy fenalcamine	50 microns (dtf) Acrylic polyurethane

## Conclusions

It is possible to classified corrosive environments qualitatively using the experience in mining who for years have been protected with paint schemes and the criteria provided by ISO 9223, ISO 12944 and ISO 14713.

Protection systems based on duplex coatings have shown great versatility, responding to the demands of the mining industry, where the cost of process shutdown is very high and the accident prevention becomes essential. This type of coating drives the performance of galvanized and paint schemes, taking advantage of their synergistic features.

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