

Copper Marine Corrosion: I. Corrosion Rates in Atmospheric and Seawater Environments of Peruvian Port

N.W. Farro¹, L. Veleva^{*2} and P. Aguilar¹

¹Universidad Nacional de Trujillo, Departamento de Química, Departamento de Física³, Av. Juan Pablo II s/n. Ciudad Universitaria, Urb. San Andrés, Trujillo, Perú

²CINVESTAV-Merida, Applied Physics Department, Carr. Ant. a Progreso, Km.6, 97310 Merida, Mexico

Abstract: The initial stages of copper corrosion behavior were studied during one year in different zones of Peruvian seawater and marine atmosphere. Several relevant factors control the development of copper corrosion process, such as oxygen content, chloride salinity, periodical cycles of drying-wetness, time of metal wetness and some specific for the region of Salaverry Port. The highest annual corrosion rate was observed in the half line of tide-water boundary (0.071 mm/year), while the lowest one was in the atmospheric zone (0.016 mm/year). The splash zone (0.025 mm/year) and full immersion (0.032 mm/year) are less aggressive for copper. The extent of copper corrosion, expressed as mass loss (C) in the marine atmospheric environment, with respect to the metal time of wetness (t), obeys the power law $C = A t^n$.

Keywords: Copper, marine atmospheric corrosion, seawater corrosion.

1. INTRODUCTION

The seawater covers more than 70% of Earth's surface and it is considered as the most abundant natural electrolyte. A great part of metallic constructions exposed in seawater and marine atmospheres are destroyed, due to the corrosion phenomenon. For the marine corrosion, the seawater is the main corrosive agent, since it is a complex solution of a great number of dissolved ionic salts, besides the additional presence of other suspended or dissolved substances, as dissolved gases, alive organic matter or in decomposition, and as a consequence its corrosiveness could increase. Usually, this water contains the ions Cl^- , Na^+ , SO_4^{2-} , Mg^{2+} , Ca^{2+} , K^+ , HCO_3^- , Br^- , Sr^{2+} , B^{3+} , F^- , Mo^{2+} (in decreasing order of their quantities) and dissolved gases (O_2 , CO_2). The percentage average of the most abundant ions in seawater (salinity 35.00%, density 1.023g/cm^3 at 25°C) is the following: 55.3% chloride, 30.8% sodium, 3.7% magnesium, 2.6% sulfur, 1.2% calcium and 1.1% potassium [1].

Seawater is a very aggressive medium for the metals and it can cause severe corrosion damages to the metallic structures in very short lapses of time and the formed corrosion products could contaminate the surrounding environment (air, sea water, alive matter, etc.). The factors that determine the type of corrosion attack on metal and its rate can be classified as chemical, physical and biological [1-7]. The most significant parameters that determine seawater corrosivity are the content of dissolved oxygen, water temperature and its flow rate, salinity and pH, likewise the biological activity (bio-deposits), as well as the environmental zone, to which the metal is exposed [2, 3]. *The dissolved oxygen* (oxidizing agent) is the most important factor in the corrosion process,

and its transport, by diffusion, towards the surface of the metal, is the decisive stage of the corrosion kinetics. The oxygen concentration in very cold waters can be as high as 11ppm [7]. The photosynthesis of green plants and the action of sea waves tend to increase the oxygen level, while the biological demand of oxygen for the decomposition of dead organisms can diminish its level. Oxygen concentration corrosion cells can be created from the deposits on a metal surface or may be due to the structural design, causing pitting or crevice corrosion, or both, at these localized sites. The effect of the oxygen concentration on corrosion is metal-dependent. For copper and its alloys, a complete elimination of dissolved oxygen can diminish its corrosion at negligible levels. In quiescent seawater, the oxygen concentration has a negligible effect on copper.

Seawater *salinity* typically varies from 32 to 37 g/kg (3.2 – 3.7 %), and generally, this degree of variation does not alter metal corrosion rates. Salts as sodium chloride (together with magnesium, potassium and calcium), represent more than 90% of the solids dissolved in the seawater and its content average is of 35 g/kg (3.5%). The salinity varies according to the intensity of the evaporation of seawater or contribution of fresh water coming from rivers: dilution of the seawater in some parts of the ocean (zone of the equatorial line) and the evaporation in others (in tropical and subtropical zones) cause movement of water between these areas. The chloride ion corrosivity accelerates pit and crevice corrosion initiation, and their propagation in metals.

From thermodynamic point of view, the raise of seawater *temperature* usually accelerates the electrochemical corrosion reactions on metals, when all other parameters remain constant. However, this condition cannot be achieved; thus, the influence of the temperature should be analyzed in function of the caused variation of the previously mentioned factors. For example, an increment of seawater temperature diminishes the oxygen solubility, and increases the biological activity, while the chemical equilibrium that involves the

*Address correspondence to this author at the CINVESTAV-Merida (Center for Investigation and Advanced Study), Applied Physics Department, Carr. Ant. a Progreso, Km.6, Cordemex, C.P. 97310, Merida, Yucatan, Mexico; E-mail: veleva@mda.cinvestav.mx

precipitation of calcium carbonate and magnesium hydroxide, is altered to increase the probability of formation of a calcareous scab, deposited on the surface of the metal (a protector layer like a physical barrier). With the temperature variations during the annual seasons, copper and many copper alloys show high rates of corrosive attack, especially during the summer months. However, in this same period, the water warming leads to an evolution of the dissolved gases, especially oxygen, likewise it favors the formation of calcareous scale on metal surface. These two factors reduce the corrosion rate. In this way, the net result is that an increment in water temperature increases several times the copper corrosion rate, however, at temperatures above 60°C, the corrosion rate declines, due to the dominant effect of the reduction in levels of dissolved oxygen. For sea areas from north to south, the corrosion of copper and its alloys is highly sensitive to the seawater temperature [8].

At the surface of open seawater, the pH is between 7.5 and 8.3, depending on the amount of dissolved carbon dioxide (CO_2) that is exchanged between water and atmosphere. Plants consuming CO_2 for photosynthesis in the day can move the pH to a higher level, while some micro-organisms can increase CO_2 by their biochemical oxidation, and move the pH to a lower level [7, 9]. Daily fluctuations in pH , from 8.0 to 8.2 do not influence on metal corrosion behavior, practically, however, they can affect the calcareous scale deposition on the metal surface, and this in turn, directly affects the corrosion rate. With the increment of pressure, pH value is decreased, so in the great depths of seawater, the creation of the incrustations (protective layers on the metal) is unlikely [2]. The pH of seawater could have lowered the values because of the presence of atmospheric pollutants (acid gases) in highly polluted coastal locations or of high industrial activity.

Many metals are significantly affected by the *flow velocity* of seawater. For example, in the case of copper, there is a critical velocity, above which the corrosion becomes excessive. However, when the velocity of seawater is less or equal to 1 m/s, copper behaves well, without any significant corrosion rate [7]. Seawater velocity can cause corrosion of special forms, such as *corrosion-cavitation*; a phenomenon resulting from the joint action of corrosion and cavitation.

The marine environment, involving seawater, includes several zones, to which the metal structure can be exposed (Fig. 1) and they determine the degree of its corrosion, and the specific corrosive attack: 1) atmospheric, 2) splash/spray, 3) tidal (high and low), 4) submerged/full immersion (shallow water and deep ocean) and 5) mud zone. During the tides, the difference in water levels can vary up to 13 m, depending on the geographic location. From the point of view of the corrosion process, the tides and splash zones are the areas where the metal is more affected by the corrosion, due to the formation of differential aeration cells [7, 9].

The seawater at the vicinity of the coast, especially in ports, can present a high grade of contamination, if intense economic-industrial activities or outlets of rivers and/or canals exist that gather great quantity of waste of the human activities. The contents of substances generated by organic degradation (as nitrates, nitrites, ammonia, sulfates, sulfurs and phosphate, among other) are part of the seawater pollution that can increase the corrosion rate of metals [10].

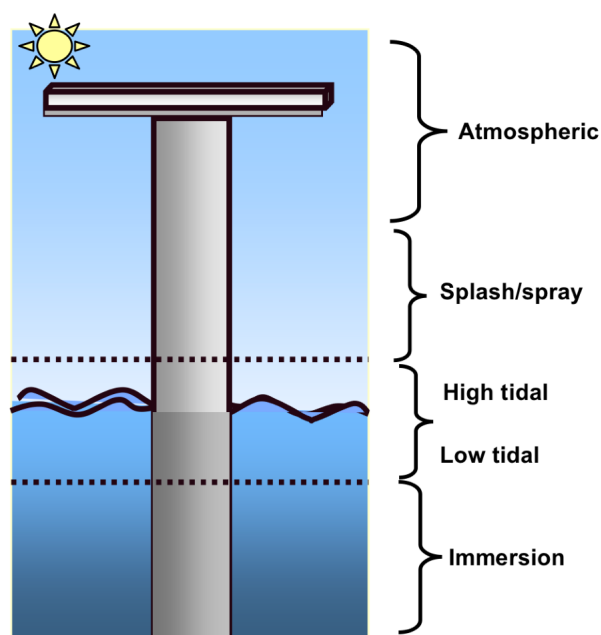


Fig. (1). Different marine zone around metallic pile of harbor structure.

Copper is one of the structural metals widely used in marine environments. In polluted atmosphere of chlorides, the copper and its alloys form thin layers of corrosion products, generally brown-greenish or green-bluish, known as patina [11-13], which protects the metal against subsequent deterioration. Copper and its alloys can also be used to submerged seawater and in seacoast where they support well the corrosive aggressiveness of the intense marine aerosol. Studies of marine corrosion of different structural metals have also been reported by Schumacher [2], including copper and its alloys, placed in different zones of marine environments, as part of the seacoasts of United States, Panama and of the northern hemisphere. Corrosion tests of copper in seawater and its aerosols have been carried out in tropical environments [14, 15].

The copper corrosion in seawater has been relatively less studied than its atmospheric corrosion, and particularly in Peru, no previous study has been carried out in this aspect. In the Peruvian region "La Libertad" ("The liberty"), one of the important northern harbors is located in the country, Terminal Portuario (TP) of Salaverry (Fig. 2), near to the city having the same name. The TP Salaverry is an artificial harbor, "pier port", which is constantly exposed to swell and tidal variations. Dredging works are permanently carried out to allow the entrance of the ships of great soaked, necessary for the port economic activities.

With the purpose of studying the hydrochemical and environmental factors consequent of the increment of the port activity in the TP of Salaverry-Peru, which can affect the rate and magnitude of the corrosion of metallic structures, samples of electrolytic copper have been investigated in different marine zones, including the Peruvian seawater of the Salaverry port. The aim of this research is to enlarge the studies on marine corrosion of copper in its initial stages, in order to establish policies of corrosion prevention, maintenance, remodeling, amplification or partial or total substitution of metallic structures, which are affected by the corro-

sive aggressiveness of the environmental factors, specific for the port TP of Salaverry.



Fig. (2). Aerial photographs of Terminal Portuario Salaverry ($8^{\circ}13'40,57''$ S; $78^{\circ}58'54,60''$ W), showing (in yellow circle and arrow) the location of the corrosion test station and the environment that surrounds it: the areas of ships and crafts are zones of continuous dredged of silts.

2. EXPERIMENTAL

2.1. Exposure of Copper Samples

During one year (September 2006 – August 2007), 144 sheet samples of electrolytic copper (99.99 mass%; $100 \times 50 \times 1$ mm), previously etched [16], have been exposed to different seawater zones (submerged, tidal and splash) and also above the free water surface, in the atmospheric one [17, 18], with the purpose of obtaining the profile of copper corrosion rates for these zones [7]. The coupons (Fig. 3) were coded, and then fixed with polypropylene fasteners, concentrically, in groups of 12, along a PVC tube of 0.27 m of diameter and 2.50 m of height [19].

Other copper samples ($150 \times 100 \times 1$ mm) were exposed in the marine atmospheric zone [18], placed in a wooden rack located at 4 m from the seawater shore on a wooden jetty and at 2.30 m on water level. The analysis of the metal samples (by triplicate) and the determination of its corrosion rates were made at 3, 6, 9 and 12 months of exposure in the different test zones. “Catchers”, i.e., devices of chloride ions (air salinity) and sulfates (as SO_2) were set on wooden rack, for determination of their monthly deposition rates, and the corrosion aggressiveness categories of the atmosphere [20-22].

2.2. Hydrochemical Parameters of Seawater

Several properties of the seawater (temperature, salinity-conductivity, content of sulfates, chlorides, nitrites, nitrates and phosphates) were monitored during the period of this test. The variations of some seawater physiochemical parameters, during the annual period of this study, are shown in Fig. (4), while Fig. (5) presents the seawater contents of phosphates, nitrites and nitrates.

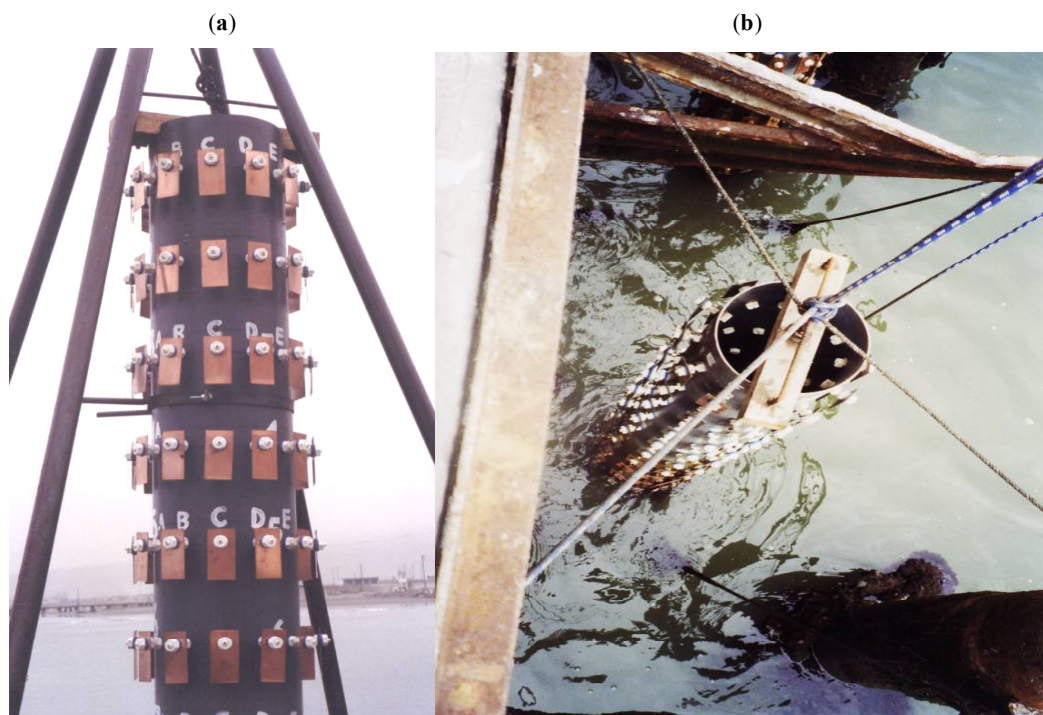


Fig. (3). PVC tube containing 144 coupons of Cu, placed in 12 levels in group of 12 for level, before being exposed in test (a); semi-submerged in seawater of the TP of Salaverry-Peru (b).

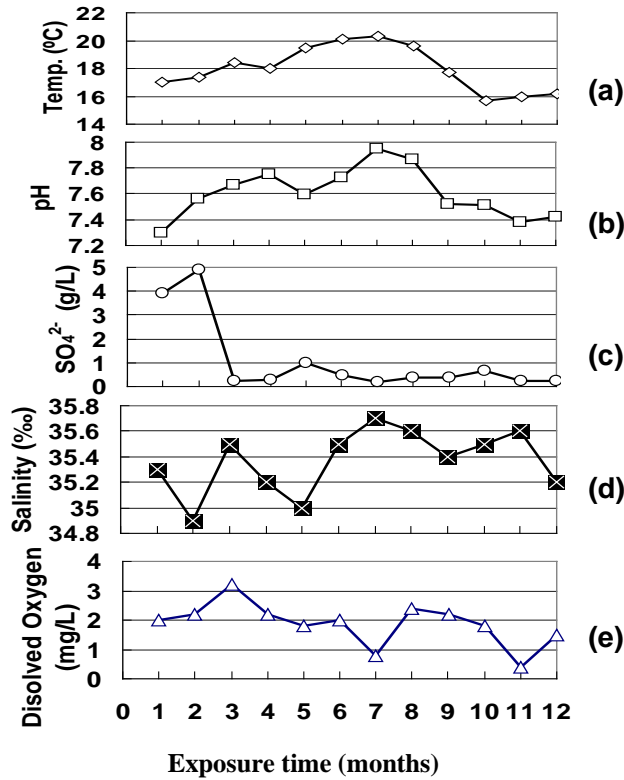


Fig. (4). Monthly variation of seawater physiochemical parameters: (a) temperature, (b) pH, (c) sulfates content, (d) salinity, and (e) dissolved oxygen. **Note:** The seasons of the year in the southern hemisphere (Peru) are opposite to those in the northern hemisphere. The measurement of the parameters is once monthly and corresponds to seawater at 2 m from the exposed samples.

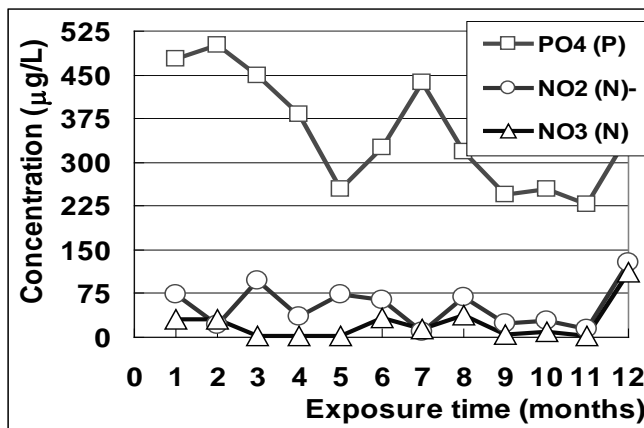


Fig. (5). Seawater content of phosphates (PO_4^{3-}), nitrites (NO_2^-) and nitrates (NO_3^-) in the Peruvian port TP of Salaverry (September'2006 - August'2007). **Note:** The measurement of the parameters is once monthly and corresponds to seawater at 2 m from the exposed samples.

A comparison between the measured concentrations (Fig. 5) and the allowed ones, according to the Peruvian Regulations of the Ministry of Fishery [23], is shown in Table 1.

It can be observed that the phosphate content (Fig. 5, Table 1) during the whole year is above the permitted maxi-

imum limit ($100\mu\text{g/L}$), except of the months of January (in summer) and May-July (in spring season). In the case of nitrites, their concentration varies between 20 and $100\mu\text{g/L}$ during the test period. However, the contents of nitrates stayed, in general, in low values, below the permitted ($300\mu\text{g/L}$), for cold waters.

Table 1. Measured Concentration Averages of Phosphates, Nitrites and Nitrates in Cold Coastal Peruvian Seawater, Compared to the Permitted by PRMF Regulations

Ions ($\mu\text{g/L}$)	Measured	Permitted
Phosphates (PO_4^{3-})	348	100
Nitrites (NO_2^-)	31	---
Nitrates (NO_3^-)	5	300

Note: Seawater temperatures: $15.7^\circ\text{C} - 20.3^\circ\text{C}$ (18.6°C average); $\text{pH} = 7.30 - 7.95$.

Values of the air relative humidity (provided by the Meteorological Bureau of the Captancy of Salaverry Harbor) were used to calculate the time of wetness (TOW) of the metallic surface [24], considered as the effective, real time for metal corrosion process [25].

3. RESULTS AND DISCUSSION

The profiles of copper corrosion rates, as corrosion penetration, calculated from the mass loss of samples, are shown in Fig. (6), which compares the values corresponding to 6 and 12 months of exposure in splash, tidal and immersion zones. The profiles (Fig. 6) indicate that the annual values of copper corrosion (12 months) are smaller than those of 6 months, except for those specimens that have been exposed

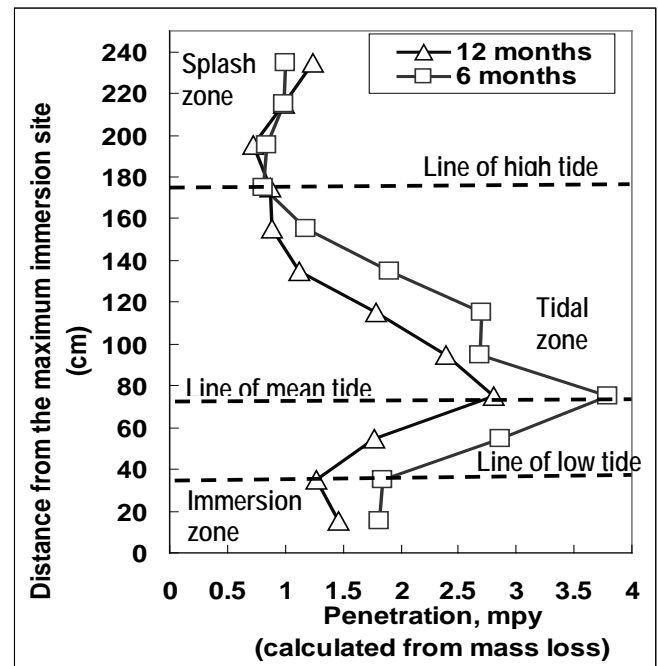


Fig. (6). Profiles of copper corrosion rates in mils (thousandths of an inch) per year penetration, corresponding to copper samples exposed in different zones of the Peruvian sea (Port TP of Salaverry).

up to the line of high tides, in the splash/spray zone, where both values (of 6 and 12 months) are very similar. Therefore, in this last zone, it can be considered that the copper *patina* (corrosion products), formed after 6 months of exposure in the presence of chlorides, has begun to act as a protective layer for the metal against the corrosion, slowing its corrosion rate within the time.

Table 2 collects the copper corrosion rates (annual mass loss) for samples exposed in three marine zones, during the annual period. The experimental data (Fig. 6 and Table 2) indicate that the highest annual corrosion rate of copper, obtained in the Peruvian marine environment of TP Salaverry, took place at the line of *mean tide*, which is 2.4 times larger than the observed in the splash zone and approximately 2 times larger than the one in the full immersion zone. The corrosion of copper in the full immersion zone is serious and even higher than that in the splash zone.

Table 2. Copper Annual Corrosion Rates (Mass Loss) in Peruvian Marine Environment in Different Zones

Zones of Marine Environment	Corrosion Rates	
	g/(dm ² Year)	mm/Year
Splash	2.23	0.025
Mean tidal (average line of water)	6.36	0.071
Full immersion	2.87	0.032

The progress in copper mass loss, corresponding to different marine zones, during the annual period of exposure is shown in Fig. (7).

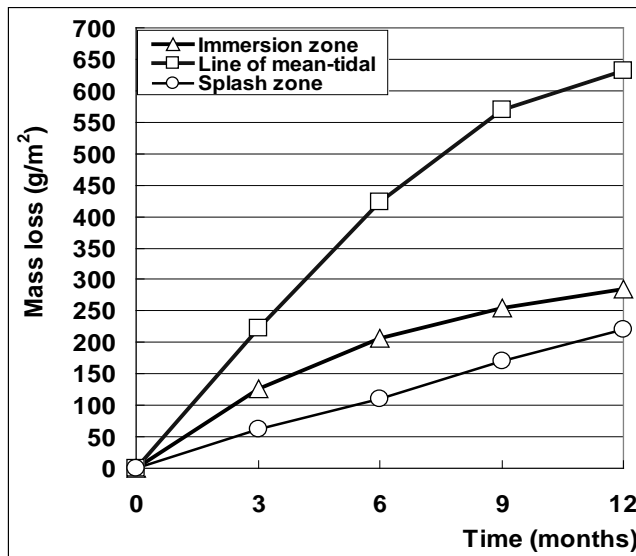


Fig. (7). Annual progress in copper monthly mass loss, corresponding to different seawater zones: splash, line of mean tide (average line of water), and full immersion zones of the marine environment (Peruvian TP of Salaverry).

The reported results (Fig. 7) reveal that the *monthly* copper corrosion rate of samples exposed in the *splash zone* keeps relatively constant (19-20g/m²) during all year, which is consistent with the results shown in Fig. (6), where copper corrosion rates at 6 and 12 months are very similar in the

splash zone. Apparently, the formed patina (corrosion products) on the copper surface are not acting as protective coating for the metal, so the corrosion progresses almost constant up to 12 months (Fig. 6). The patina presents porosity and low adhesion to the metal and these facts favor the diffusion of corrosive agents and moisture toward the metal surface, which is a necessary component for the operation of the multiple corrosion cells. This is the reason why the patina (mass loss) grows almost *linearly* and does not have a parabolic behavior, which is the typical law of growth of effective protective layers [26].

3.1. Copper Corrosion at the Water Boundary – Mean Tidal Line

The experimental data shown in Fig. (6) reveal that when copper is exposed in the tidal zone, its corrosion rate increases up to maximum in the *mean tidal zone* (average line of water), with a value of 2.8 times larger than that observed in the *high tidal zone* with corrosion rate values similar to those obtained for copper in the splash zone. The *low tidal zone* is less corrosive for copper and the corrosion rate is similar to that experimented in the full immersion zone. Visual observations of the metal surface revealed that the patina layer formed the first months on the samples, exposed to the mean tidal zone, can be easily removed, which means that it has not a good adhesion to the metal and the corrosion process has been facilitated in this way. This fact and the higher oxygen content above the water boundary, besides the constant wetness of the metal surface, are the main factors that accelerate the copper corrosion in this zone. However, it seems that after six months of exposure (Fig. 7), the copper corrosion progress tends to decrease at this stage, when probably the diffusion of aggressive agents through the aqueous surface film and the layer of corrosion products (patina) become the limiting factor that controls the copper corrosion rate. Once a good surface film of patina is formed, the corrosion rate continues to decrease over a period of year. The annual value of copper corrosion rate in the mean tidal line (Table 2) is 6.37 g/dm²year (0.071mm/year), a value that is almost 4 times larger than those compiled by Schumacher [2] for copper in the mean tidal line of tropical seawaters. However, this annual corrosion value (Table 2) is within the range of rates 0.02-0.10 mm/year, achieved in the same marine zone, reported by Uhlig [7], and in the average of 1.8 g/m²d [14].

It is important to note that sometimes ship and boat vessels leave oil residues, which can be tenuously observed on the water surface: the oil film can keep suspended the sand particles that ascend on the sea surface from the marine bottom, due to the processes of dredging. The sand particles could act as a weak abrasive on the copper surface exposed in the tidal zone, removing part of the formed patina and retarding its stable formation on the metal surface, so the copper corrosion progress is faster in this zone (high curve slope in Fig. 7).

3.2. Copper Corrosion in the Full Immersion Zone

The progress in copper mass loss (corrosion rate) of samples exposed in the immersion zone is shown in Fig. (7). It can be noted that the magnitude of corrosion rate is larger than that of copper exposed at the splash zone, and the kinetics of the corrosion process presents a *parabolic behavior*,

which suggests the presence of a protective layer of patina on the metal surface, because the copper rate descends with time down to 2.88 g/dm²year (0.032 mm/year; 0.78g/m²d). This annual corrosion rate is about 2.5 times larger than the value compiled by Schumacher [2], but in the range of values (0.79-1.56 g/m²d) reported in tropical waters [14]. Similar magnitudes of copper corrosion rates (0.02 to 0.07 mm/year), for the samples completely submerged, have been reported by Uhlig [7]. Therefore, the copper corrosion annual value in the immersion zone, found in this research, is within the Uhlig's magnitudes and it also has a similarity to that presented by Shreir *et al.* (0.034mm/year) [26]. It can be considered that in the immersion zone the factor that controls the copper corrosion rate is the content of dissolved oxygen and its diffusion process, towards the metal surface, through the layer of formed patina (corrosion products). On the other hand, due to the biological activity existing in the seawater, the copper samples present areas of biomass deposits since the third month of exposure in the immersion zone that forms additional barrier for the copper corrosion process progress (Fig. 8).

3.3. Atmospheric Corrosion of Copper

3.3.1. Airborne Pollution and Time of Wetness (TOW)

During the annual exposure period of copper samples, in the marine atmosphere of Port Salaverry, the average rate of chloride deposition was 255.8 mg/m²d (Fig. 9), which locates the corrosive aggressiveness of this atmosphere in the S2 category ("high"), according to ISO 9223 [24]. The highest level of salinity is measured in January (summer season), followed by September and July, when the corrosive cate-

gory of atmospheric aggressiveness is in a higher level S3 ("very high").

The monthly deposition rate of sulfur compounds (estimated as SO₂), during the annual test period, is shown in Fig. (10). The monthly average of deposition was 5.53 mg/m²day, that makes the corrosive aggressiveness of the marine atmosphere of TP Salaverry in the category P1 ("very low"), according to ISO 9223 [24]. Reported study suggests that above a threshold value of 62-68mg/m²day, the copper corrosion rate increases considerably with the level of pollution [27].

The monthly values of the time of wetness (TOW) that the samples have received during the test period, are shown in Fig. (11). The annual value of TOW has been larger than 5500 h and for that, the corrosive category of atmospheric aggressiveness of the marine environment of TP Salaverry is located in the category "C5" ("very high"), according to ISO 9223 [24].

The direction and velocity of the prevailing winds, during this period of study, have been 2-6 m/s in the spring (eastern, south-eastern and southern) and almost 3 m/s in the summer, with similar wind directions to the previous ones. In autumn, the wind sporadically increases to 4-5m/s, being the most frequent winds from the east and south-east. The winter cold fronts from north-east and west-north-east create higher wind velocity up to 6 m/s. The winds coming from east drag mainly sand from the dunes that surround the marine port of Salaverry, while those coming from south mainly carry the marine aerosol.

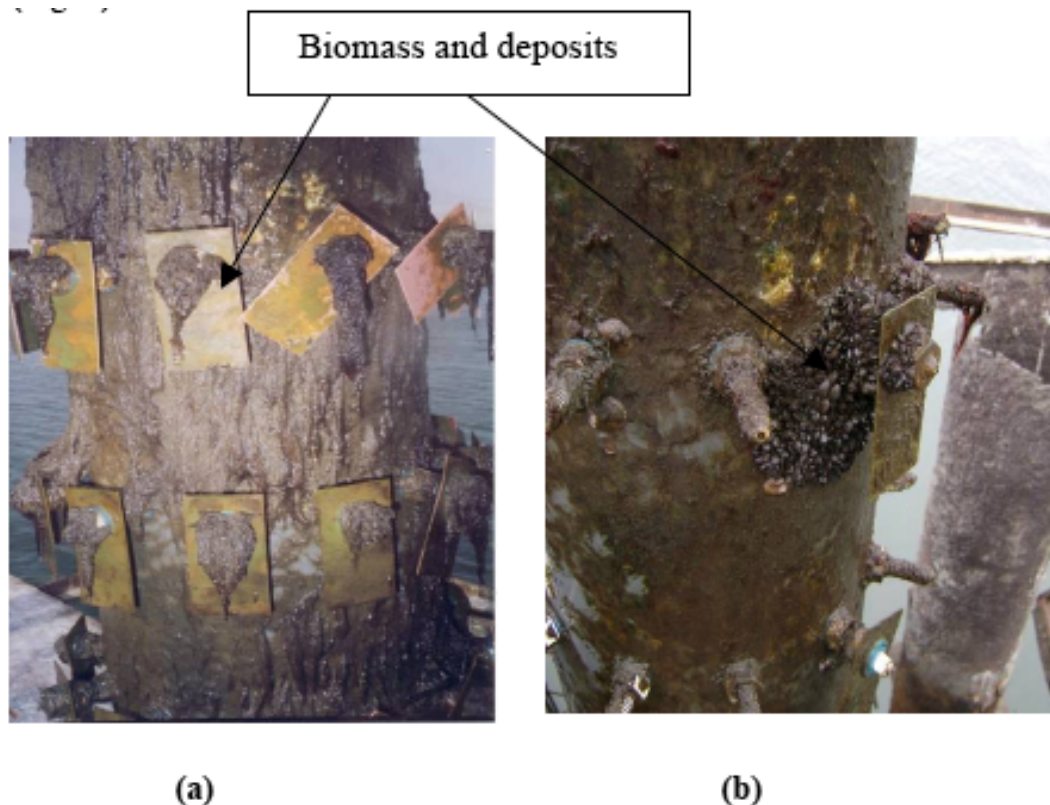


Fig. (8). Copper samples exposed in the immersion zone: (a) biomass formed after 3 months of exposure; (b) deposits on barnacles stuck of the tube and on the copper samples after 12 months of exposure.

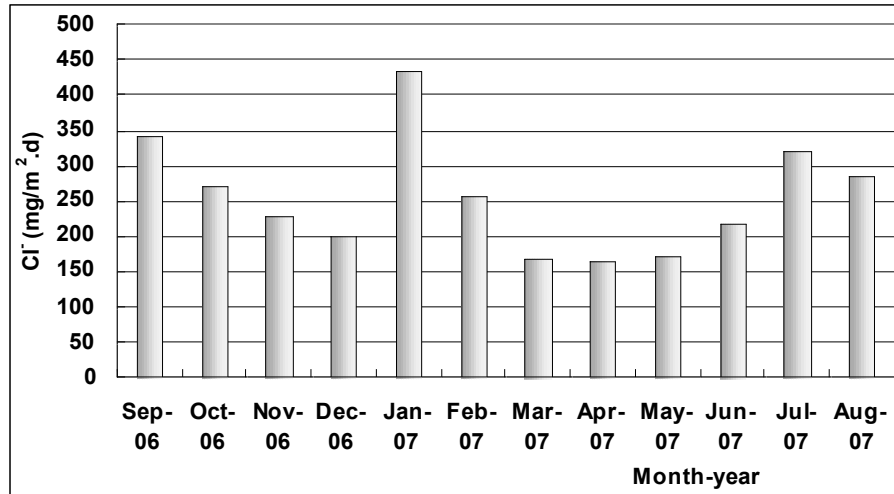


Fig. (9). Monthly deposition rate of chlorides in the marine atmosphere of the Peruvian port of Salaverry (September 2006 – August 2007).

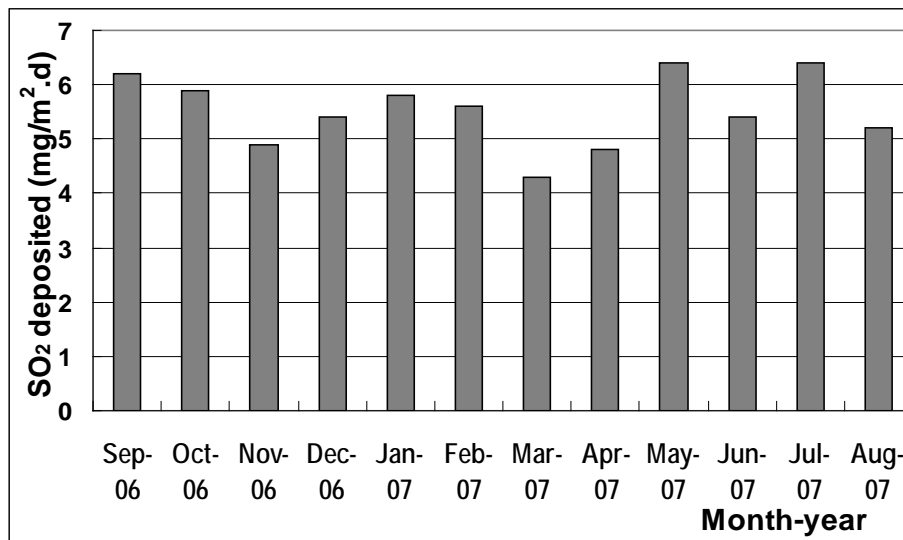


Fig. (10). Monthly deposition rate of sulfur dioxide (SO₂) in the marine environment of the Peruvian port of Salaverry (September 2006 – August 2007).

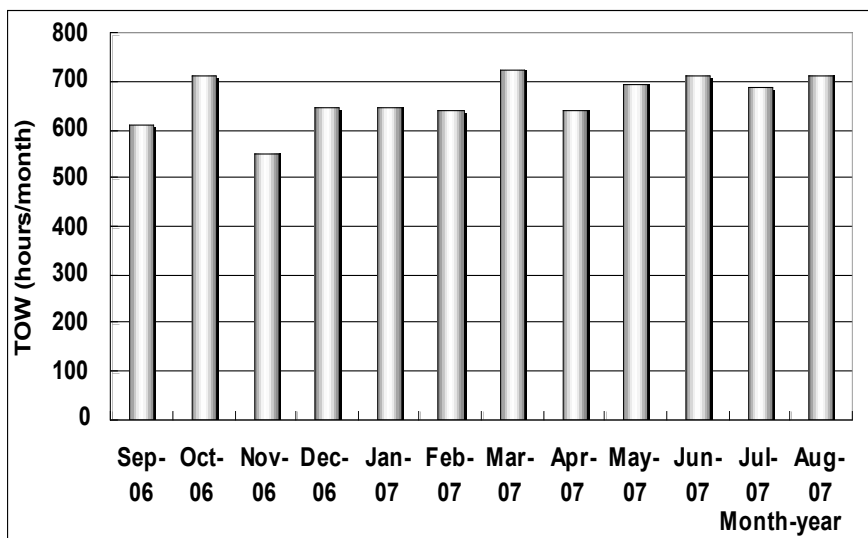


Fig. (11). Monthly values of time of wetness (TOW) in the marine environment of the Peruvian port of Salaverry (September 2006 – August 2007).

3.3.2. Copper Corrosion Kinetics

There are two ways to represent the extent of corrosion (C) expressed by the mass loss of the metal: as a function of exposure time (Fig. 12) or related to metal time of wetness (t), corresponding to each exposure period (Fig. 13). Thus, the TOW was substituted for the exposure time as being the real time of the corrosion process. During the first six months, the corrosion rate is almost constant (Fig. 12), followed by gradual decreasing in the posterior months of test period, probably due to the physical barrier exerted by the formed patina (copper corrosion products) on the metal surface.

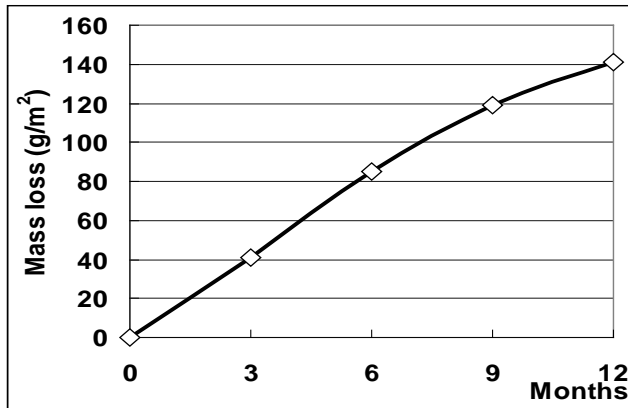


Fig. (12). Copper atmospheric corrosion rate (mass loss) during the annual exposure in marine environment of Peruvian port of Salaverry.

The analysis shows that the relation between A (annual mass loss) and t , during the atmospheric exposure of copper samples, could be described by the power equation $C = At^n$, where A is the annual mass loss corresponding to annual TOW, and n is the exponent (Fig. 13). The experimental data present very high correlation coefficient ($R \geq 0.95$) values of $A = 150.41 \pm 1.06 \text{ g/m}^2\text{year}$, while $n = 0.87 \pm 0.07$. Similar equations have been reported earlier by several authors and obtained for atmospheric corrosion of copper exposed to tropical humid climate in different environments [28].

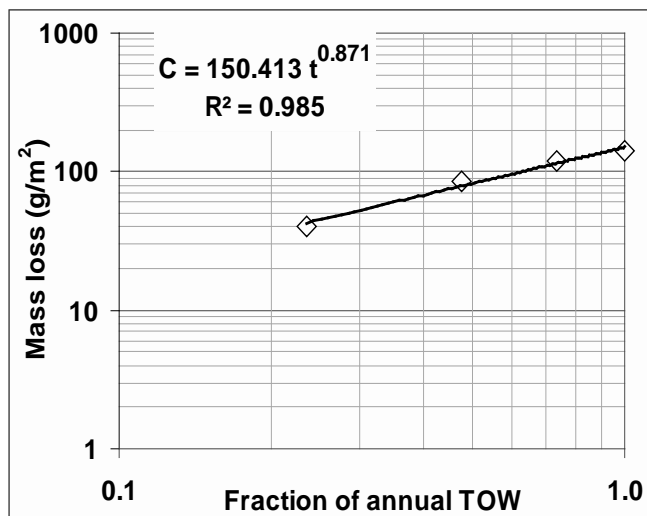


Fig. (13). Copper atmospheric corrosion (mass loss) versus fraction of annual time of wetness received in the marine environment of Peruvian port of Salaverry.

When comparing the progress of copper corrosion rates in different marine zones (Figs. 7, 12; Table 2), the experimental data indicate that the lowest ones are obtained in the atmospheric marine environment (0.016mm/year) and they are close to those of the splash zone (0.025 mm/year). The corrosion rate of copper was found to be serious in the full immersion zone (0.032 mm/year) of the Peruvian port sea area, being two times larger than that in the marine atmosphere. In the atmospheric environment, the metal surface suffers cycles of drying and wetness, and due to this the corrosion process is interrupted periodically. Something similar occurs in the splash zone and for this reason there is a similitude in copper corrosion behavior. Schumacher also concludes that the corrosion behavior of copper and its alloys in the splash zone is more nearly to the atmospheric than to the full immersed one [2].

CONCLUSIONS

- The annual corrosion rate of electrolytic copper, in different zones of Peruvian seawater and marine atmosphere, in a growing order, has been increasing in the following way: atmospheric zone (0.016 mm/year), splash zone (0.025 mm/year), full immersion zone (0.032 mm/year), and with the largest value (0.071 mm/year) in the half line of tide – water boundary.
- Several relevant factors control the development of the copper corrosion process in different marine zones: the oxygen content in the immersion zone; the time of wetness, chloride content (salinity) and the periodical cycles of drying-wetness in the atmospheric and splash zones; partial removing of copper patina layer and its adhesion to the metal, in the half line of tide. Additional factors, such as sand carried by the wind, continuous dredging made in coastal areas and boarding, deposits of biomass on the surface of metal, and oil residues, influence the magnitude of the corrosion rates.
- The progress in copper mass loss (C) in the marine atmospheric zone, with respect to the metal time of wetness (t), obeys the power law $C = At^n$. Something similar occurs in the splash zone and for this reason there is a similitude in copper corrosion behavior.

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