ATMOSPHERIC CORROSION: THEIR PREVENTION BY COATINGS (PROJECTS MICAT & PATINA, CYTED)

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ABSTRACT

The Ibero-American Map of Atmospheric Corrosiveness (MICAT) project was set up in 1988 sponsored by the International Ibero-American Programme "Science and Technology for Development (CYTED)". Fourteen countries have been involved in the project: Argentina, Brazil, Chile, Colombia, Costa Rica, Cuba, Ecuador, Mexico, Panama, Peru, Portugal, Spain, Uruguay and Venezuela. Research has been conducted both at laboratories and in a network of 72 atmospheric exposure test sites throughout the Ibero-American region, thus considering a broad spectrum of climatological and pollution conditions. This paper presents a summary of some of the results obtained in one-year atmospheric exposure testing of carbon steel, zinc, copper and aluminium: corrosion rate, morphology of attack of the base metal and of the corrosion products formed, their nature and electrochemical properties.

The Thematic Network "Anti-Corrosion Protection of Metals in the Atmosphere" (PATINA) was constituted in Lisbon in December 1994, upon the finalization of the MICAT project. The network is participated by the fourteen countries mentioned above plus Bolivia. One of the main tasks of this network is to evaluate the corrosion protection behaviour of a wide range of conventional and advanced coatings in typical atmospheres of the Ibero-American region. This paper presents an overview of the organizational structure of the network and of the coating materials being studied.

KEYWORDS: atmospheric corrosion, low-carbon steel, zinc, copper, aluminum, coatings.

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INTRODUCTION

In January 1988, the 4th General Assembly of the International Ibero-American Programme "Science and Technology for Development (CYTED)" approved the project "Ibero-American Map of Atmospheric Corrosiveness (MICAT)". Administrative and organization details of the CYTED program were given in previous papers [1-2].

Among the objectives to be fulfilled in the MICAT project the following are of special interest:

(a) increasing the present knowledge on the mechanisms of atmospheric corrosion,
(b) developing mathematical relations to predict atmospheric corrosion from climatological and contamination parameters,
(c) drawing up the Ibero-American Map of Atmospheric Corrosiveness (MICAT project), and
(d) elaborating practical guides for optimal selection of metals and coatings (conventional and advanced) in function of the atmospheric aggressiveness. This aim is considered in a second part of the paper (PATINA project), where a variety of protective systems are being tested in a network of representative atmospheric corrosion stations.

The objective (c) is not covered in this paper

In August 1988, the working group that was to realize the project was formed in Caracas. Initially, it was composed by the following countries: Argentina, Chile, Colombia, Mexico, Panama, Peru, Portugal, Spain and Venezuela. Costa Rica and Cuba joined the project at the second coordinators meeting held in Rio de Janeiro (June 1989). Finally, Ecuador and Uruguay joined the group at the third annual meeting in Costa Rica (September 1990), and Bolivia in the seventh annual meeting in Portugal (December 1994).

The research group in each participating country is made up of specialists in atmospheric corrosion from research institutions, universities and private companies. One representative acts as coordinator of the research group and attends the general meetings of the project that are held periodically. The general meetings were held in Caracas (1988), Rio de Janeiro (1989), Costa Rica (1990), Buenos Aires (1991), Madrid (1992), Santiago de Chile (1993), Lisbon (1994), and Cuzco (1995).

PROJECT MICAT

EXPERIMENTAL PROCEDURE

Although with its own peculiarities, the project basically follows the outline of the ISOCORRAG [3] and ICP/UNECE [4] projects, with the aim of a desirable link between the three projects. Standardized procedures ISO and ASTM have been followed.

Figure 1 shows the location of the Ibero-American network of atmospheric corrosion test stations. The names and some environmental features of the test sites are listed in [5]. As can be seen, the network provides a variety of climatological and pollution conditions.

The atmosphere at each test site is characterized from meteorological and atmospheric pollution data (ISO 9223, ASTM G92). The former include basically the temperature, relative humidity (RH) of the air and rainfall. These parameters are recorded at the station itself - most lie in meteorological stations of the Meteorological Service of the country in question - or at a neighbouring meteorological station. The recorded thermohydrograms are used to show the time of wetness (TOW), the fraction of the year in which RH ≥ 80% and T > 0°C. The deposition rates of SO_2 and chloride are measured following ISO 9225 (ASTM G91). Average annual environmental data have been published elsewhere [5].

Fig. 1.- Network of atmospheric corrosion stations.

The materials investigated are structural metals, in the form of flat plate specimens, with the following features: steel (unalloyed, low carbon); zinc (98.5% min); copper (99.5% min), and aluminum (99.5% min). Some countries are also testing hot dip galvanized steel. The test specimens are usually 10 x 15 cm^2 and cut out from 1 mm thick sheets.

The exposure sequences include: 3 one-year exposures, one two-year exposure, one three-year exposure, and one four-year exposure (Fig. 2). In the paper only preliminary 1-year exposure data are reported.

Four specimens of each material are exposed in each sequence, three of which are used to determine weight losses according ISO 9226 (ASTM G1).

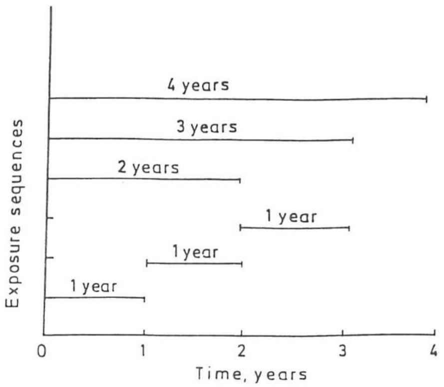

Fig. 2.- Diagram of exposure sequences.

The removal of corrosion products by chemicals to determine the weight loss involves a loss of valuable information of the atmospheric corrosion process. Therefore, a fourth specimen (Fig. 3) of each sequence was used for laboratory studies: (a) analysis of the corrosion products by means of diverse experimental techniques: XRD, IR, Mössbauer spectroscopy, water-soluble contaminants, etc.; (b) microscopical examination (surface and cross-section) of the morphology of the corrosion products layers; and (c) electrochemical studies: polarization resistance, impedance spectroscopy, electrochemical noise, etc.

Identification of corrosion products

This information was also obtained, whenever possible, from the corrosion products collected from the three samples used for weight-loss measurements, before their immersion in the corresponding pickling solutions.

The identification techniques used were basically the following: X-ray diffraction (XRD), Infrared electroscopy (IR) and Mössbauer Spectroscopy (only for the steel). In certain cases elemental information was also obtained by Energy Dispersive Spectroscopy (EDS). The techniques used are complementary. The integration of all of them has permitted a more precise identification of the corrosion compounds formed.

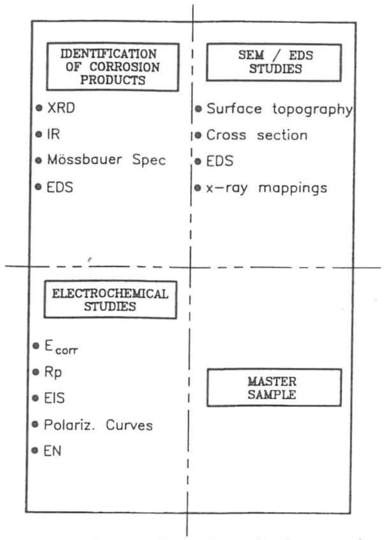

Fig. 3.- The fourth specimen. Discontinuous lines show the four sections in which the specimen was divided to carry out different laboratory studies to obtain additional information of the corrosion processes.

Morphology of the attack of the base metal and microstructure of the corrosion products

This information was obtained from observation with the Scanning Electron Microscope (SEM) of both the outer surface of the layer of corrosion products and cross-sections. In some cases elemental information was also obtained by EDS, as well as X-ray mappings of certain chemical elements of interest (mainly S and Cl).

Electrochemical studies

The aim of these studies was to obtain information about the corrosion behaviour and protective characteristics of the different materials covered with their corrosion products.

These studies were conducted in the presence of an electrolyte of 0.1 M Na_2SO_4. This is a conductive medium, of low aggressiveness, which allows electrochemical measurements to be made and which can to a certain extent simulate the atmospheric corrosion process in the presence of visible layers of humidity.

Different electrochemical techniques were applied, according to the facilities of the different laboratories: corrosion potential (E_{corr}), polarization resistance (Rp), electrochemical impedance spectroscopy (EIS), polarization curves, cyclic voltametry, electrochemical noise (EN), etc. In this paper we shall only make reference to Rp values (Table 1), the technique most used by the different participating countries. R_p measurements were carried out after 1, 24 and 48 hours of immersion in the electrolyte, applying a pulse of 20 mV and recording the current response when this reached an asymptotic value.

Table 1.- Synthesis of electrochemical data.

Material	Unexposed samples, Rp (KΩ.cm^2)			Exposed samples Rp (KΩ.cm^2), 1hr
	1 hour	24 hours	48 hours	
Steel	4.35	3.15	2.48	0.50
Zinc	0.70	0.75	1.16	5.0
Copper	6.72	23.6	35.2	25*
Aluminium	409	1003	844	1000*

*In marine atmospheres Rp values are much lower, 5 times for copper and 50 times in the case of aluminium.

Master sample

One part of each specimen was kept as control for the bank of specimens collected in the laboratories of the project coordinator. With these control specimens it has been possible to confirm the information provided by the different laboratories, to take photographs of the colouring, morphology, structure, etc. of the corrosion products, and to quantify soluble species within them, mainly chlorides and sulphates [6].

RESULTS

Correlation between corrosion data and meteorological and pollution parameters

In an ASTM STP publication [5] an attempt was made to correlate corrosion data with meteorological and pollution parameters. Table 2 shows a synthesis of some of the relationships obtained.

Table 2.- Relationships between the annual corrosion data and the environmental parameters

Equations	Remarks
$C_{Fe} = 0.012\ P + 0.94\ S + 1.06\ Cl - 3.9$ (R = 0.78) (Eq. 1) $C_{Zn} = 2.73\ TOW + 0.017\ Cl + 0.03$ (R = 0.65) (Eq. 2) $C_{Cu} = 0.049\ RH + 0.03\ S + 0.01\ Cl - 2.57$ (R = 0.69) (Eq. 3) $C_{Al} = 1.32\ TOW - 0.07\ T + 0.03\ S + 0.008\ Cl + 0.94$ (R = 0.67) (Eq. 4)	C_{Fe} = carbon steel annual corrosion (μm) C_{Zn} = zinc annual corrosion (μm) C_{Cu} = copper annual corrosion (μm) C_{Al} = aluminium annual corrosion (g/m^2)) T= temperature annual average (°C) RH = relative humidity annual average (%) P = annual precipitation (mm) TOW = time of wetness (annual fraction) S = SO_2 pollution annual average (mg SO_2/m^2.d) Cl = chloride pollution annual average (mgCl$^-$/m^2.d) R = multiple correlation coefficient

By using binary interaction terms together with the main effect terms of the environmental variables, the fits did not improve substantially. Only a low improvement of 10% were found in the best cases (mild steel and zinc).

The variance accounted for in the regression equations decredased sharply if the statistical treatment was applied to rural atmospheres only (Table 3), which was in agreement with results obtained in a previous paper [7].

Table 3.- Relationships between the annual corrosion of low-carbon, zinc, copper and aluminium in rural atmospheres and the environmetal parameters

Materials and number of data	Equations	Remarks
Steel (N = 13)	$C_{Fe} = 0.90\ T - 3.41$ (R = 0.48) (Eq.5)	C = annnual corrosion (in μm for steel, zinc and copper, and g/m^2 for aluminium) T = temperature annual average (°C) RH = relative humidity annual average (%) TOW = time of wetness (annual fraction) R = multiple correlation coefficient
Zinc (N = 35)	$C_{Zn} = 3.04\ TOW - 0.06$ (R = 0.63) (Eq.6)	
Copper (N = 37)	$C_{Cu} = 0.02\ RH - 0.80$ (R = 0.52) (Eq.7)	
Aluminium (N = 36)	$C_{Al} = 0.33\ TOW + 0.06$ (R = 0.33) (Eq.8)	

Atmospheric corrosion of low-carbon steel [8]

Corrosion in practically unpolluted rural atmospheres is usually less than 20 μm/year. In atmospheres of this type the concentrations reached by SO_2 and Cl^- pollutants are usually less than 10 and 3 mg/m².d, respectively. Of the phases present in the corrosion products there is a predominance of lepidocrocite (γ-FeOOH) with the presence also of goethite (α-FeOOH). The layers of corrosion products are usually thin, as corresponds to low corrosion rates, showing cracking in their different strata (Fig. 4).

In urban and industrial atmospheres the SO_2 concentration can be relatively high. In consequence, soluble sulphate concentrations among the corrosion products are greater than in rural atmospheres. The main corrosion products in this type of atmosphere continue to be lepidocrocite and goethite, with the predominance of the former.

With regard to marine atmospheres it is useful to distinguish between them those whose Cl^- content is moderate (<60 mgCl$^-$/m².d) from others, know as coastal, and very close to the coastline, in which the Cl^- concentration can be extremely high. Annual steel corrosion in sites in the first group is between 20-60 μm while corrosion rates in the second group reach values of more than 60 μm/y. A frequent extra loss of steel thickness in this second type of atmosphere is due to exfoliation phenomena, whereby the corrosion products flake off. Among the corrosion products, in addition to the two crystalline phases already mentioned (lepidocrocite and goethite), two new phases usually appear, akaganeite (ß-FeOOH) and magnetite (Fe_3O_4), the latter in the strata of the rust layer closest to the base steel.

The results obtained using electrochemical techniques infer a lack of protective value in the corrosion products formed in the different atmospheres (Table 1). This is consitent with the fact that the layers of corrosion products are highly cracked (Fig 4). The cracks are formed due to the formation of voluminous corrosion products at the metal/rust interface during periods of humidification; subsequent drying periods promote cracking.

Atmospheric corrosion of zinc [8]

The corrosion rate of zinc in atmospheres whose Cl^- content is less than 60 $mg/m^2.d$ generally remains below 2 μm/year, and is even lower (<1 μm/year) in rural atmospheres. In marine atmospheres, and especially in coastal sites, corrosion reaches greater levels of attack. With regard to the species which constitute up the corrosion products, a band may be established around 20 $mgCl^-/m^2.d$. For salinities lower than this level the corrosion products are usually formed by zinc oxides (zincite) and basic zinc carbonates (hydrozincite). For salinities greater than this level there is a presence of basic zinc chlorides (simonkolleite).

In rural atmospheres, and in consonance with the light attack experimented by zinc in these sites, a discrete and isolated appearance of white zinc oxide products (zincite) products was observed on the uniform layer of hydrozincite (Fig. 4). In urban atmospheres the formation of corrosion products is more abundant. However, sulphur compounds, which doubtless are formed, are not detected in appreciable amounts because they are leached by rain water due to their hydrosoluble character. In industrial atmospheres it is not rare to see localized attacks at the zinc base. In marine atmospheres there is a formation of acicular corrosion products of basic chlorides (hydroxichlorides), along with the zincite formations (Fig. 4), promoting intense and localized attacks below the layers of corrosion products.

With regard to the electrochemical measurements (Table 1), the tendency of the corrosion rate to decrease with immersion time in the saline solution used leads us to infer that the corrosion products have a certain protective value.

Atmospheric corrosion of copper [8]

In rural atmospheres the copper surface is at first quickly covered by a film of cuprous oxide (cuprite, Cu_2O), the predominant corrosion product. In time, it is possible and quite frequent to see the formation of brochantite, basic copper sulphate, in spite of the low levels of SO_2 present in this type of atmosphere. The low solubility of these compounds, and the fact that they are not leached by rain water, facilitate their detection. These crystalline products, present as fines or coarser particles (Fig. 4), appear on the protective Cu_2O film in open structures of low compactness. The corrosion rate remains below 1 μm/year and the soluble sulphate and chloride contents are relatively

high, again confirming the tendency of this metal to fix both pollutants from the atmosphere.

In urban and industrial atmospheres cuprite continues to be the predominant corrosion product, always accompanied by basic copper sulphates. Within the latter, brochantite is predominant, though at times posnjakite is also observed. This product is always conjugated with brochantite and in time takes its structure. The morphology of the corrosion products in this type of atmosphere is highly similar to that shown in rural atmospheres not polluted with SO_2 and Cl^-. The corrosion rate of copper in this type of atmosphere is usually between 1 and 2 μm/y, though in industrial atmospheres heavily polluted with SO_2 corrosion may reach greater levels of attack. In all of the atmospheres the electrochemical measurements suggest the formation of corrosion products with a certain protective value (Table 1).

With regard to marine atmospheres in addition to cuprite it is also common to identify atacamite and a pratacamite, an isomorphous compound of atacamite which in time is transformed into atacamite. Other corrosion products may also be present but were not identified due to their low concentration or low crystallinity. The surface morphology of the layer of corrosion products is highly similar to that presented in the rest of atmospheres, though the presence is somethimes detected of acicular products corresponding to copper hydroxichlorides. The layers of corrosion products have a low protective nature, are poorly constituted (with open structures of low compactness with abundant internal porosity, thus explaining the high corrosion rate of copper in this type of atmosphere, >2 μm/year, as confirmed by electrochemical measurements (Table 1).

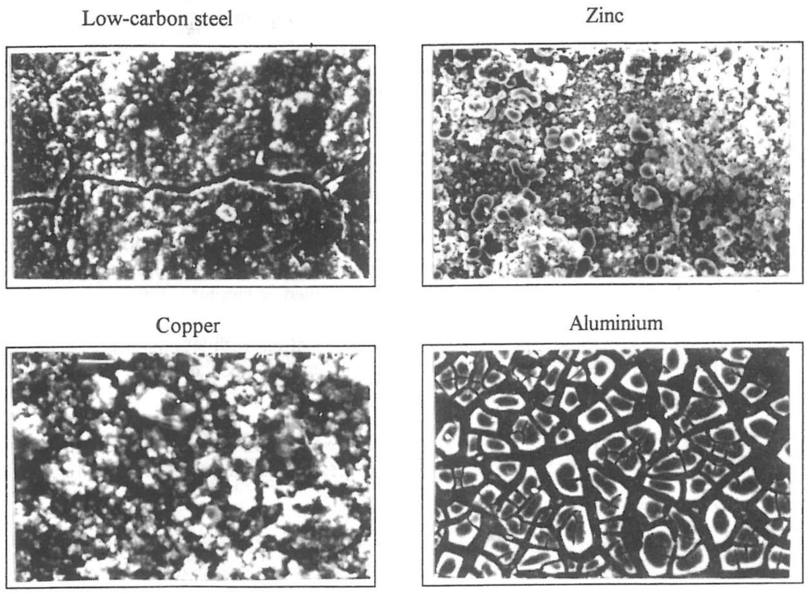

Fig. 4.- SEM micrographs of weathered surfaces.

Atmospheric corrosion of aluminium [8]

In rural and urban atmospheres (not polluted with Cl^-) aluminium remains practically unaltered. Corrosion rates are insignificant (<0.5 $g/m^2.y$). The insignificant amount of corrosion products therefore made their detection difficult. With the scanning electron microscope and electronic microprobe only airborne dust particles (silicates) were observed, discretely distributed across the surface. Practically no soluble sulphates and chlorides were found among the corrosion products. The very high values of Rp shown by aluminium in this type of atmosphere (Table 1) confirm the passivating nature of the corrosion products.

In industrial atmospheres aluminium shows a differential behaviour dependant on the specific characteristics of this type of atmosphere. Aluminium corrosion in this type of atmosphere can go from practically nil (similar to rural or urban atmospheres) to a considerable degree of attack if the atmosphere contains chemical species aggressive to aluminium, such as halides.

In marine atmospheres aluminium corrosion (>1.0 $g/m^2.y$) is dependent on atmospheric salinity, acquiring the form of pitting which can affect large percentages of the exposed surface. The amount of corrosion products formed on the metal surface allows for their detection. XDR permits the detection of poorly crystallized aluminium oxides and IR reveals the presence of hydroxyl groups. On the surface of the aluminium focal points of intense attack (pitting) are detected, together with zones which, though without pitting, present cracks in the passive layer of alumina. The corrosion products tend to crack as the alumina loses its hydrating water. Such cracking is highly evident and is shown in Fig. 4. Rp values are lower in this type of atmosphere than in others, explaining the existence of perforations (pitting) in the passive layer (Table 1).

PATINA THEMATIC NETWORK (ANTI-CORROSION PROTECTION OF METALS IN THE ATMOSPHERE)

The main objectives of this network are as follows(9):

(a) To define a common methodology throughout the Ibero-American region for identifying and evaluating the corrosion behaviour of conventional and advanced coatings in different atmospheric conditions. This is an objective shared with other international bodies, such as the United Nations Economic Commission for Europe (UNECE), International Standards Organization (ISO), etc. which are currently engaged in similar efforts.

(b) Formation of groups to work on these issues in countries with less developed scientific and technical know-how in this field. There is currently a need for such activities in these countries, and

(c) To define areas of interest in which specific pre-competitive research projects and innovation projects (IBEROEKA) may be carried out in the forthcoming years with companies in the sector.

In order to set about objective (a) it is necessary to take as a starting point a collaborative test with the intervention of the different Associate Units of the countries participating in the Network. The results of this prospective test will constitute in themselves a preliminary information base of great value for national R+D centres and companies involved in this area (technology transfer), information which is not available at the present time.

Organizational structure

15 countries in the region are participating in the proyect: Argentina, Bolivia, Brazil, Chile, Colombia, Costa Rica, Cuba, Ecuador, Mexico, Panama, Peru, Portugal, Spain, Uruguay and Venezuela.

In the final meeting of the MICAT project in Lisbon (December 1994) the 15 participating countries took the opportunity to define the thematic content, organizational structure and other details of this collaborative programme.

Internally the project is structured around 6 working groups defined on the basis of the different protective materials to be tested. The coordination of each working group is the responsibility of renowned specialists within the region. In accordance with a series of guidelines, these 6 experts prepared a proposed plan of action for each one of the groups. The proposed plans were partially agreed in the Lisbon meeting and definitively approved in the Cusco meeting (December 1995).

The approved organizational structure is presented in Figure 5.

Test sites

Obviously it is not envisaged in this case to carry out experimentation in the 75 testing stations which comprised the MICAT network, but in a representative sample of them selected in accordance with the following criteria: a) coverage of the different atmosphere types, b) testing stations best equipped and with an operative capacity during the development of the collaborative programme, c) their distribution among the different participating countries, and d) their belonging to an international network. Table 4 shows the working groups and test sites according to types of atmosphere involved.

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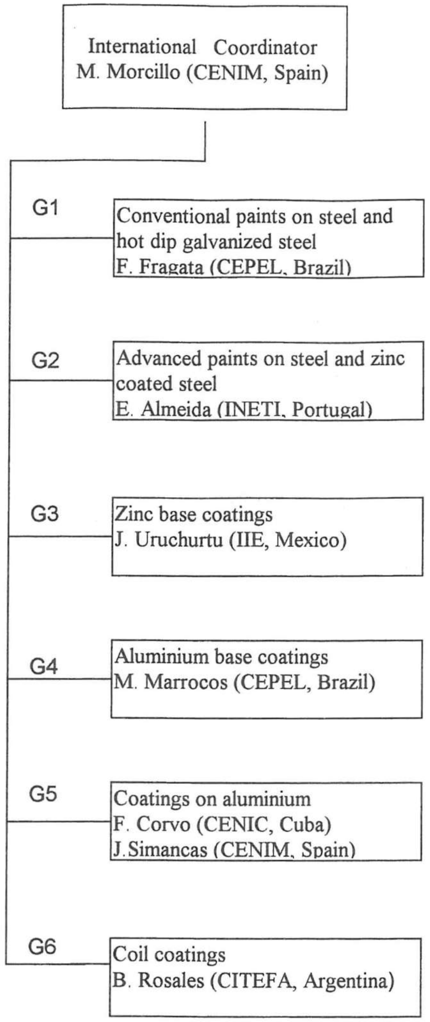

Fig. 5.- Organizational structure of the collaborative programme "EVALUATION OF THE BEHAVIOUR OF ANTI-CORROSION COATINGS IN ATMOSPHERES IN THE IBERO-AMERICAN REGION"

Table 4. Working groups, types of atmosphere and test sites.

Groups	Types of atmosphere/ test sites				
	Rural	Urban	Industrial	Marine	Coastal	Special
G 1	San Pedro (Col) Pardo (Esp)	Cerrillos (Chl) Lumiar (Prt)	Cubatao (Bra)	Tablazo (Ven)	Sines (Prt)	Artigas (Ury) Quivicán (Cub)
G 2	San Pedro (Col) Pardo (Esp)	Cerrillos (Chl) Lumiar (Prt)	Cubatao (Bra)	Tablazo (Ven)	Sines (Prt)	Quivicán (Cub)
G 3	Cuernavaca (Méx) Cuzco (Per) Pardo (Esp)	Sao Paulo (Bra) La Paz (Bol)	Esmeraldas (Ecu)	Bahía Solano (Col) Colón (Pan)	Cojímar(Cub) P. Limón (Cri)	La Voz (Ven) Arenal (Cri)
G 4	Cuernavaca (Méx) Cuzco (Per) Pardo (Esp)	S. Paulo (Bra) La Paz (Bol)	Esmeraldas (Ecu)	Bahía Solano (Col) Colón (Pan)	Cojímar(Cub) P. Limón (Cri)	La Voz (Ven) Arenal (Cri)
G 5	Pardo (Esp)	Lima (Per) Lumiar (Prt) Panamá (Pan)	Esmeraldas (Ecu) Cubatao (Bra)	P. Este (Ury) Tablazo (Ven)	Viriato (Cub)	La Voz (Ven) Jubany (Arg)
G 6	Pardo (Esp)	Lima (Per) Lumiar (Prt) Panamá (Pan)	Cerrillos (Chl) Cubatao (Bra) Esmeraldas Ecu)	P. Este (Ury)	Viriato (Cub)	La Voz (Ven) Jubany (Arg)

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EFFECTS OF TETRA-ALKYLAMMONIUM SALTS ON THE POLAROGRAPHY OF Cd^{2+}, Zn^{2+} AND Mn^{2+} IN WATER

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ABSTRACT

The addition of *tetra*-alkylammonium salts, namely *tetra*-methylammonium, *tetra*-ethylammonium, *tetra*-butylammonium and *tetra*-hexylammonium salts, to the supporting electrolyte, in the presence of different metal ions, does not change the observed cathodic current for shorter carbon chains. However, an important effect is observed when **$n \geq 4$** (number of carbon atoms of each chain). This is shown through the polarograms which were recorded for different solutions of cadmium, zinc and manganese ions, in the presence and absence of those ions.

The interpretation based on electrocapillary curves has shown that electron transfer through the double-layer becomes more difficult as the length of the carbon chain increases.

Polarographic and electrocapillary experiments were followed all over.

Keywords: *Tetra*-alkylammonium salts; Polarography; Electrocapillary curves; Cadmium; Zinc; Manganese