

Fig.2.3. Dependence of the current densities, anodic  $J_a$ , maximum  $J_m$ , passivation  $J_p$  on pH for  $PO_4^{3-}$  0.2M solutions.

### 3. CONCLUSIONS.

- Current densities maximum  $J_m$  are scarcely dependents with pH.
- Current densities passive  $J_p$  became more unstable as the solution's acidity decreases. These current densities are nearly constant for basic pH.

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## CORROSION IN SEA-COAST: COLLECTION AND DETERMINATION OF MARINE ATMOSPHERIC CHLORIDES

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### 1.INTRODUCTION

Atmospheric corrosion has been studied theoretically, in the laboratory (by simulated or accelerated tests) and in field exposure tests. These types of studies complement each other, but the last one is very important to know the atmospheric conditions to metal corrosion. Some regions of the World, as for example USA or URSS, are well studied. In Europe, some countries have also studied the atmospheric conditions to metal corrosion, but other countries, such as Spain, begin now to start work in this field.

The atmospheric corrosion of metals is greatly influenced by meteorological conditions, such as humidity, temperature and its variations, wind, rainfall and dew point. These factors influence the formation of the electrolyte layer on the metal surface, which is responsible for atmospheric corrosion. In addition to the meteorological conditions, the chemical composition of air has a great importance, specially the presence of chlorides and sulfur dioxide. The first one is always present in sea-coast and harbours atmospheres and the second one is present when these places are near from industrial areas which produce pollution. The chlorides arise mostly from the sea and return to the ground fundamentally by precipitation by rain and by dry fallout. Both rain and dry deposited chlorides represent an aggressive factor for metallic structures. As rain water is not retained in the flat inclined samples used currently in atmospheric corrosion tests sites, total chloride collected seems therefore more relevant than the amount rain-borne, in trying to correlate corrosion rates with atmospheric chlorides.

Two main methods to collect chlorides from the atmosphere have been described in the literature: the "wet candle" method (1) and the "collecting metallic trough" method (2). However there are not enough bibliographic information to compare the

atmospheric salinity values measured by means of both methods in the same conditions. A comparative study of these two methods was done, four years ago, in order to provide some information about this matter(3). As an extension of that experimental study, correlation between chloride content as determined by the "wet candle" method and "collecting trough" method is exposed in the present work. Both procedures are considered in a high aggressive marine-industrial environment of the Mediterranean Spanish coast during the years 1986 and 1987. Sulfur dioxide, which can accelerate the corrosion action of chlorides, was present in that sea-coast and was collected and analyzed. Corrosion of mild steel in the same atmospheric conditions was considered too.

## 2. EXPERIMENTAL

Experiments were carried out with the "wet candle" device and the "collecting trough" device(3). The "wet candles" method consists in the collection of chlorides through a collecting 2,5 cm diameter glass tube surrounded by surgical(hydrophile)gauze, which is kept moist by immersion in a 6% glycerine-water solution contained into a 500 cm<sup>3</sup> volume erlenmeyer. The gauze was periodically changed and chlorides were analyzed monthly by Mohr method, giving the results in mg NaCl.m<sup>-2</sup>.day<sup>-1</sup>. In the "metallic collecting trough" method a 600 cm<sup>2</sup> stainless steel sheet with angle was used, collecting chlorides and rain water into a 3 litres polietilene flask. Chlorides were also analyzed monthly by Mohr's method.

Both collecting devices "under the roof" and "without roof" were oriented to the South and placed about 150 meters from the sealine in the beach of Badalona, industrial town next to Barcelona.

Sulfur dioxide was collected as indicated by British Standard BS 1747, Part 4(1969), giving the results in mg SO<sub>2</sub>.m<sup>-2</sup>.day<sup>-1</sup>.

On the other hand, 100x40x3 mm mild steel sheets samples were exposed in the same conditions, in order to study its corrosion in comparison with the chlorides and sulfur dioxide contents in that atmosphere.

## 3. RESULTS AND DISCUSSION

The results of collection and determination of chlorides - with both methods and the collection and determination of sulfur dioxide (as SO<sub>2</sub> are shown, respectively, in Fig. 1 and Fig. 2.

Fig.1. Chloride concentration during 1986 and 1987.

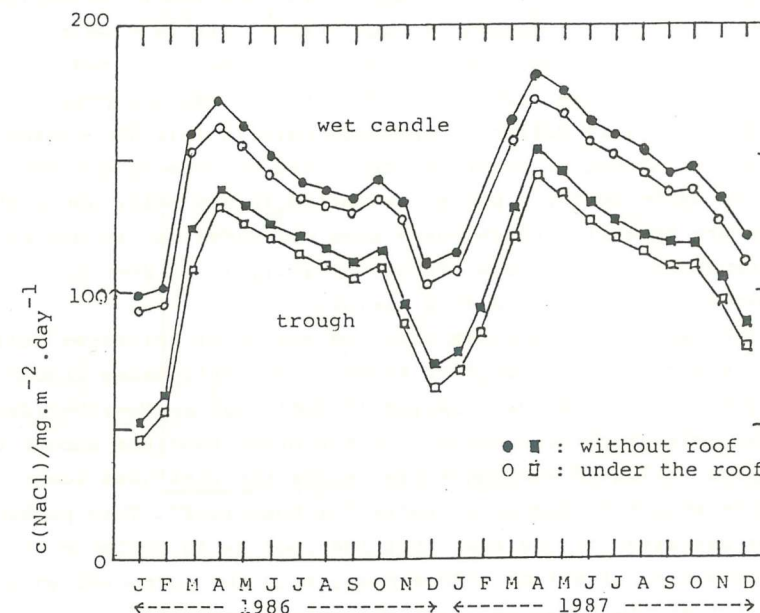
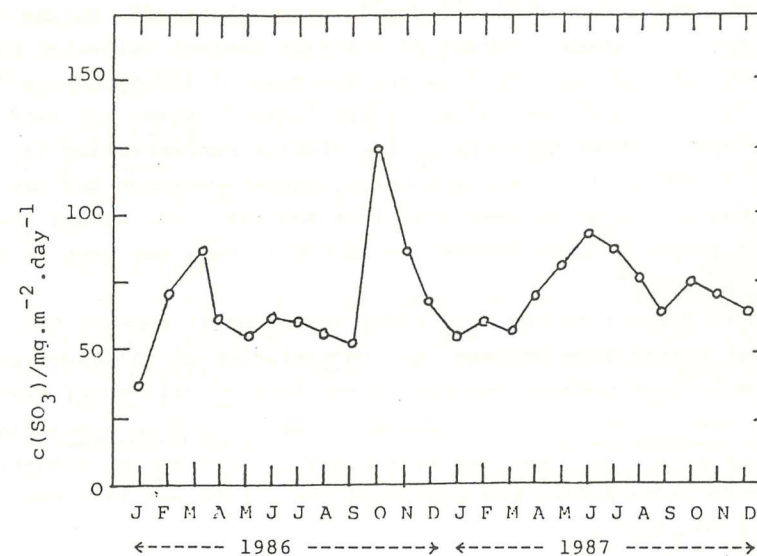


Fig.2. Sulfur dioxide during 1986 and 1987.





As can be seen in Fig.1, the amount of chlorides collected through "wet candle" method is higher than the amount collected through "collecting metallic trough" method. This is true for both different tests of the two methods: "under the roof" and "without roof". All these results corroborate the results obtained by several authors in different environments (3)(4)(5). The reason of the largest amount of chlorides collected by "wet candle" method could be explained by a better retention in the moist gauze than in the dry metallic trough, where some chlorides can return to the atmosphere by the wind action, specially if it does not rain frequently during the exposure period.

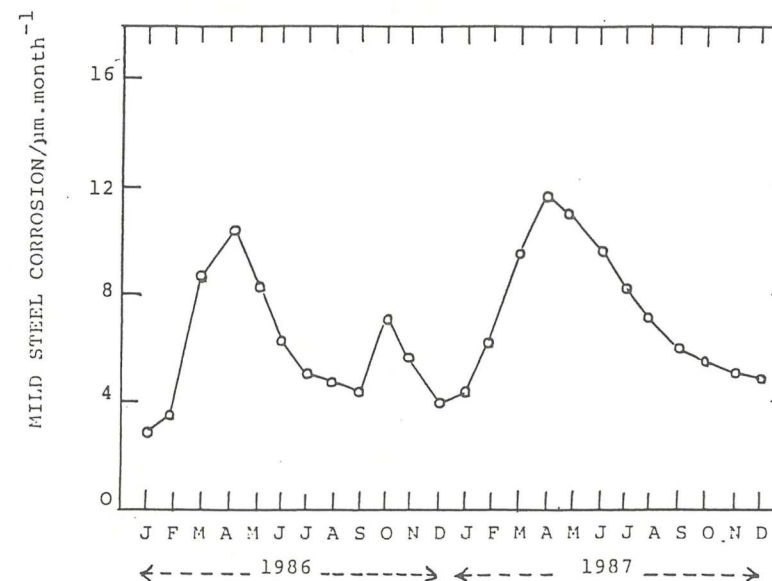
The same figure 1 shows that the amount of chlorides collected through both methods ("wet candle" and "collecting trough") is higher in March to June (Spring season) than in November, January and February (Winter season). On the other hand, the amount of chlorides collected through tests "under the roof" was lower than the amount collected by tests "without roof". This perhaps can be explained by the fact that the roof is an obstacle to the collection of all chlorides present in the surroundings of both devices ("wet candle" and "collecting trough").

The annual average of chloride content collected by means of "wet candle" method has been of  $160 \text{ mg NaCl.m}^{-2}.\text{day}^{-1}$  "without roof" and  $130 \text{ mg NaCl.m}^{-2}.\text{day}^{-1}$  "under the roof". On the other hand, the annual average of chloride content collected by means of "collecting trough" method has been of  $100 \text{ mg NaCl.m}^{-2}.\text{day}^{-1}$  "without roof" and  $95 \text{ mg NaCl.m}^{-2}.\text{day}^{-1}$  "under the roof".

Figure 2 shows that the sulfur dioxide concentration is higher in the periods: February-March, October-November and May-July than in the other months of 1986 and 1987. The annual average of sulfur dioxide content collected (as  $\text{SO}_3$ ) has been of  $60 \text{ mg SO}_3.\text{m}^{-2}.\text{day}^{-1}$ .

With respect to the mild steel corrosion, it appears that there is correlation between the concentration of chlorides collected by both methods and the weight loss of mild steel exposed in the sea-side site in each mentioned period, as shows Fig.3. The annual corrosion rate of mild steel in this marine-industrial environment during the mentioned years 1986 and 1987 has been of  $80 \text{ }\mu\text{m}.\text{year}^{-1}$ .

Fig.3. Corrosion of mild steel during 1986 and 1987.



Finally, it appears that also there is correlation between the concentration of chlorides collected by the "collecting trough" method and the corrosion of nickel coatings samples placed in this sea-side site (6).

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