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Corrosion rate evolution in concrete structures exposed to the atmosphere

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Abstract

The data on corrosion rate values measured on-site in real size concrete structures are scarce, while the data bank of values in laboratory specimens is relatively larger. The majority of the experiments in the laboratory have been performed in chambers of controlled relative humidity and temperature, however real outdoor climate usually is characterized by day–night and seasonal temperature cycles. These cycles, or natural weathering, influence the internal relative humidity of the concrete and the corrosion rate of the steel. In the present paper, results of corrosion rate of steel in chloride containing concretes exposed to natural weathering, are presented.

Four main weather events have been identified to influence the corrosion rate of reinforcements due to the changes of the hydrothermal situation of the concrete: (a) day–night cycles, (b) seasonal cycles, (c) extreme temperatures and (d) rain periods. In unsheltered conditions it is the rain (moisture content of the concrete) which controls the corrosion rate. In concretes sheltered from rain it is the temperature the controlling factor of the moisture content and then, of the corrosion rate. Moisture is well represented by the electrical resistivity. A pure Arrhenius trend of the corrosion rate could not be found because several counter balance effects develop when temperature changes. The resistivity is the parameter that more comprehensively represents the corrosion rate.

Keywords: Corrosion rate; Weathering; Reinforcements; Chlorides

1. Introduction

The alkalinity of concrete is a strong passivator of the steel. However, it corrodes when due to action of chlorides, or of a drop in pH induced by carbonation. The further evolution of the corrosion rate values has been studied from some time ago [1] by means of the polarization resistance technique. It is well established that the moisture content of the concrete is the main parameter controlling the rate of the process [2]. Thus, when the concrete is dry, the corrosion shows negligible values (below 0.1 $\mu A/cm^2$]. These values increase when the humidity goes [3] up to maximum values of around 100 $\mu A/cm^2$ (in sea water).

In spite of the effect of moisture in the corrosion is well established, very few data have been published on the influence of the climatic changes, and in particular of the temperature, T, on the corrosion rate [4,5]. All the studies reported in the laboratory have been made in controlled conditions of relative humidity, RH and T. Only recently, data have been published [6–10] on the effect of the natural climatic day–night cycles on the corrosion rate, I_{corr}. In [6] it was found that the variations of I_{corr} seem not to follow any specific trend. This behaviour was attributed to the fact that in natural conditions, the RH and T are in continuous change inside the concrete and equilibrium is not achieved.

In the present paper the study is continued and additional results on concrete specimens are presented. They help to understand the complex multiple effect that continuous temperature cycles induce in the corrosion process.

2. Experimental

2.1. Preparation of specimens and materials

In the previous paper [6], the lack of relationship between internal relative humidity and corrosion rate in

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a concrete beam contaminated with 3% of $CaCl_2$ exposed to Madrid climate (later described) unsheltered from rain was reported. In the present paper further experiments have been performed in the same beam and in concrete specimens having 3% NaCl added in the mix.

The concrete beam is shown in Fig. 1. It has been fabricated with 360 kg/m^3 of OPC and a w/c ratio of 0.7, 3% of $CaCl_2$ per weight of cement was added to the mix to promote corrosion. The beam was fabricated outdoors and water-cured during 3 days. It was then exposed to the action of the climate unsheltered from rain.

The shape of the specimens containing 3% NaCl added in the mix is shown in Fig. 2. They were cylindrical, of 7.5 cm × 15 cm in size. They were fabricated with 300 kg/m^3 of an OPC and a w/c ratio of 0.6. They were cured under water during 3 days and after exposed during one year to different fixed T and RH, in laboratory chambers. During this exposure, holes were drilled in the specimens in order to obtain a cavity in which the internal RH (RH-IN) could be measured. The

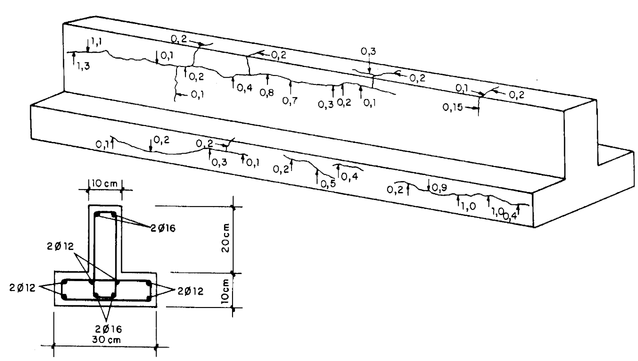

Fig. 1. Shape and crack pattern of the beam having admixed 3% $CaCl_2$ by weight of cement used in the experimentation.

Fig. 2. The specimens used in the experimentation.

type of specimens with the cavity is shown in Fig. 2. After one-year period at a constant T and RH, one set of the specimens was submitted to natural weathering. During this time, the internal (IN) and external (EXT) RH, T and weight, W, changes were measured at different periods.

2.2. Techniques

In the beam, the corrosion potential, (E_{corr}), the resistivity (ρ) and the corrosion rate (I_{corr}), were measured by means of a portable corrosion rate meter, Gecor 06, having sensorized confinement of the current [11]. The reference electrode used is $Cu/CuSO_4$.

In the specimens, the same corrosion parameters were measured by means of a laboratory made potentiostat SVC-2 [12] which uses a potentiostatic step waiting 30 s for making the measurements and applies the current interruption method for measuring the ohmic drop. The reference electrode is a saturated calomel electrode. The relative humidity, RH, and temperature, T, were recorded either in the external atmosphere and in cavities of the concrete made for this purpose [13].

The resistivity measured in both cases is an average of that of the cover. The resistivity will present a gradient from the concrete surface following moisture penetration or releasing, however the value of the resistivity, as measured with an external auxiliary electrode, is an average of that gradient, both with the portable corrosion rate meter and the potentiostat.

2.3. Methods of concrete moisture measurement

For measuring the RH and T, a Vaisala portable hygrometer has been used [10]. This probe has been frequently calibrated by means of introducing it in recipients of standard salt solutions. During the one-year period, no appreciable deviation has been found in the probe, which had a rather quick response and short stabilisation time.

It is well known [5,9,10] that the measurement of RH-IN is not an easy task, because in order to obtain a reliable value, it is necessary to wait until stabilisation of the probe reading. This stabilisation may take minutes or hours depending on the previous reading and, mainly, if the value itself is high (RH > 90%) may take more than 24 h to stabilise. However, in concretes exposed outdoors, the temperature changes may proceed very rapidily due to the day–night evolution and accordingly the RH evolves which makes unfeasible an exact reading of this last parameter unless permanent sensors are installed. That is, in outdoors exposure RH measurements may not be exact due to temperature evolution during day cycles.

Therefore, the procedures finally adopted were alternatively one of the following:

(a) to maintain the probe permanently inserted in the cavity, this enables a smooth evolution and gives enough accurate values,

(b) when the permanent insertion was not feasible, the probe was previously stored in similar RH in order to avoid sharp changes needing long stabilisation time (15 min resulted enough in these cases) and

(c) when stabilisation during a reasonable time was not possible, RH-IN values at 1–5 and 10 min were registered and graphically extrapolated to longer times using a logarithmic expression previously deduced.

2.4. Weathering

The beam has been held outdoors submitted to all weather events, however the concrete specimens have been submitted to sheltered or unsheltered conditions in function of the particular aspect to be studied. The concrete specimens have also been submitted to artificial freezing and raining to reproduce that natural weathering.

The following events were particularly studied:

- effect of extreme temperatures: freezing below 0°C and heating at 40°C,
- direct submission to natural or artificial rain,
- drying after rain and
- sheltered from rain.

Madrid has a climate with relatively well-marked seasons. It has a dry atmosphere which reaches values between 10% and 30% RH-IN during summer where the rain appears seldom. Autumn and spring may be relatively mild (averaged $T \cong 15$°C with intermittent rain periods, and winter temperatures are usually around 10°C, although seldom temperatures below 0°C and snow periods, may appear.

3. Results

3.1. Beam containing chlorides

Fig. 3 shows the record of the temperature (T) variations during two years in the external (T-EXT) atmosphere and inside the cavity (T-IN) of the beam. It can be seen that IN and EXT values of T are very similar.

However, this is not the case with the relative humidity, RH (Fig. 4). As has been previously reported [3–14], while the external day–night RH changes are significant, inside the beam the RH remains more stable. The RH are lower in spring–summer and higher in autumn–winter following the major events of raining and T evolution.

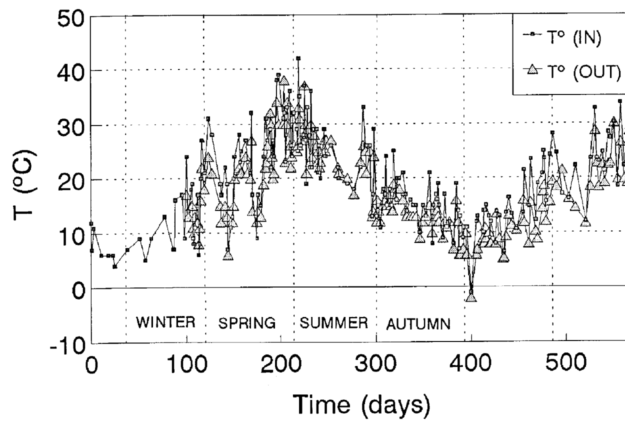

Fig. 3. Evolution of temperature in the atmosphere ambient of the beam and in its interior (in a cavity).

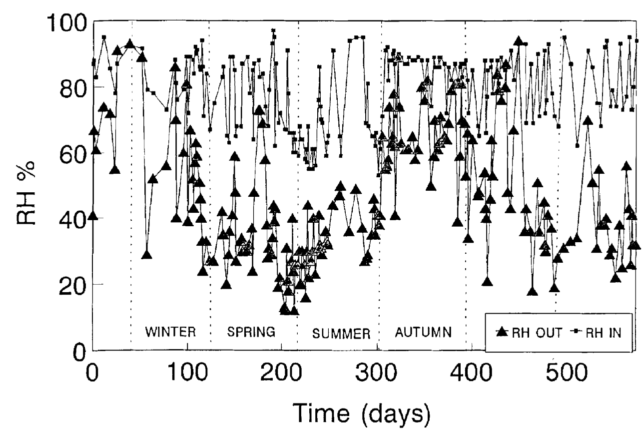

Fig. 4. Evolution of relative humidity in the atmosphere ambient of the beam and in its interior (in a cavity).

The combined effect of T and RH can be better visualized in Fig. 5 where the RH inside the beam cavity and outside have been plotted in a psicrometric abacus. Each point represents the mean RH during each month of the year, over two years. It can be seen that in the external atmosphere the changes in temperature induce significant changes of RH since the total humidity remains unchanged. However, inside the cavity, the temperature changes induce phenomena of condensation–evaporation which enable the RH to remain much more constant.

As was already mentioned [6], Fig. 6 indicates that no precise trend can be identified in I_{corr} during the two years testing. It appears that RH and T do not have any direct relation to the corrosion rate. This is better visualized in Fig. 7 where the I_{corr} has been plotted versus the RH-IN.

In order to ascertain the corrosion behaviour in more detail, some particular weather events were studied: rain and T evolution along the day–night cycle. Thus Fig. 8

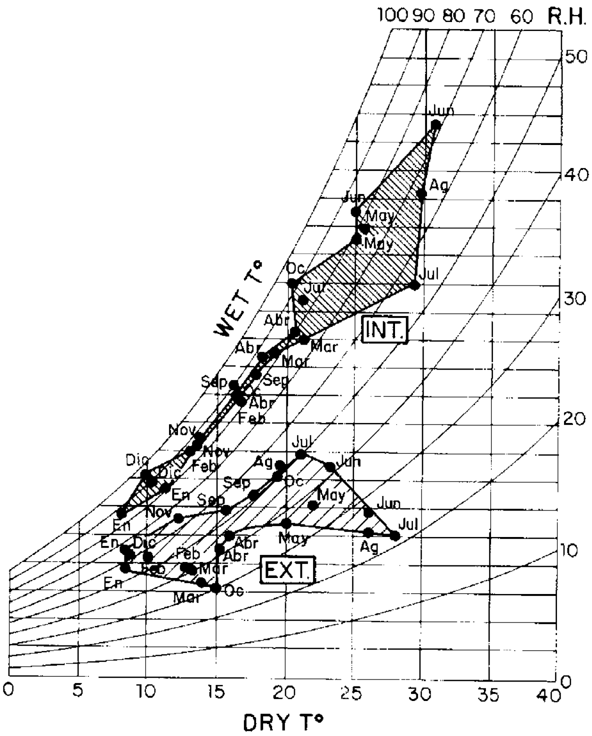

Fig. 5. Psicrometric abacus of the evolution of *T*/RH-EXT and *T*/RH-IN of the beam. Each point is the mean of a month. The total duration of the recording has been two years.

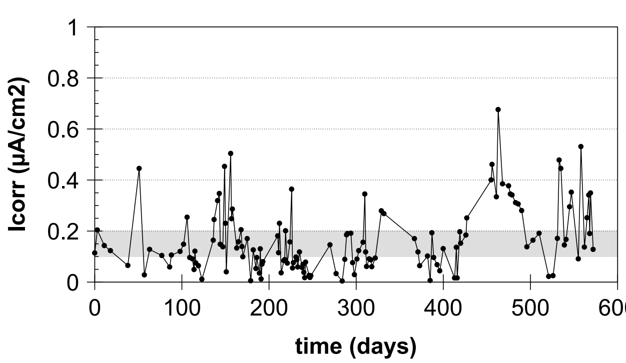

Fig. 6. Evolution of the corrosion current, I_{corr}, of the rebar of the beam during two years.

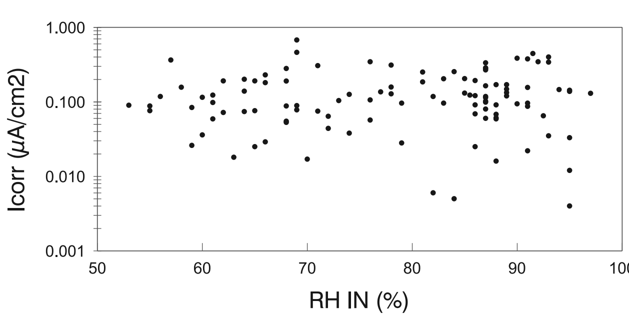

Fig. 7. Relation between I_{corr} and RH-IN of the beam.

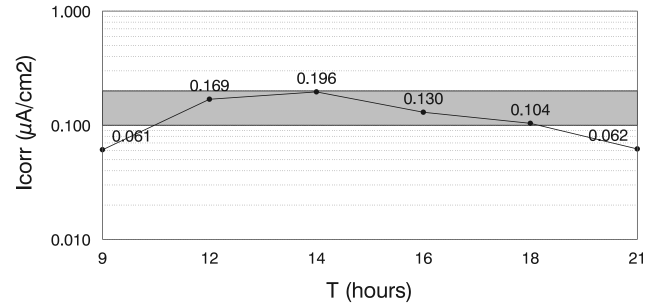

Fig. 8. Evolution of I_{corr} of the reinforcement of the beam during 12 h, starting from 9 a.m. to 9 p.m. The increase during midday indicate the dependence of I_{corr} with the increase in temperature.

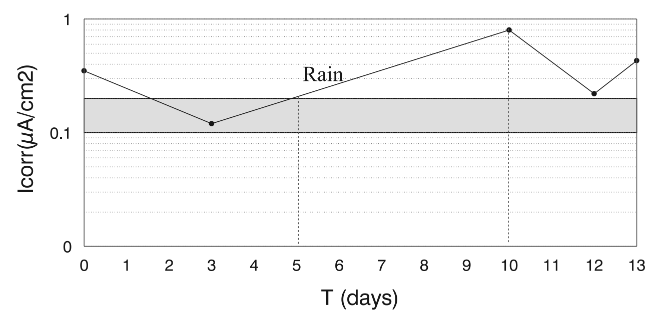

Fig. 9. Evolution of I_{corr} before and after a rain event. The rain occurred on day 5 and the maximum in I_{corr} was detected on day 10.

depicts the changes in I_{corr} during a single day from the morning to the evening. It is clear here that the *T* has an effect on the I_{corr} from which it can be concluded that in the short-term daily cycle, the *T* does influence the I_{corr}.

In a similar manner the effect of rain periods has been studied. Thus, in Fig. 9 an example is shown of how after raining (day 5 in the figure), a high I_{corr} value was noticed (day 10 in the figure). Therefore, a higher humidity also induces a higher corrosion rate.

3.2. Small specimen

In Fig. 10 the values of *T*/RH-EXT have been represented, while in Fig. 11 those inside the specimen, *T*/RH-IN, are depicted together with other parameters: weight (*W*), I_{corr}, E_{corr} and resistivity (ρ).

As a general trend, it can be deduced from Figs. 10 and 11 that the *T*-IN and *T*-EXT are similar and therefore not much attention will be paid to their differences.

However, the RH-IN evolves in a quite different manner than RH-EXT and therefore will be commented in detail. With regard to the weight, it was not always measured, although enough data were collected to analyse its trend.

Period 1: The changes suffered by the *T* and RH-IN when submitted to daily cycles were studied during this

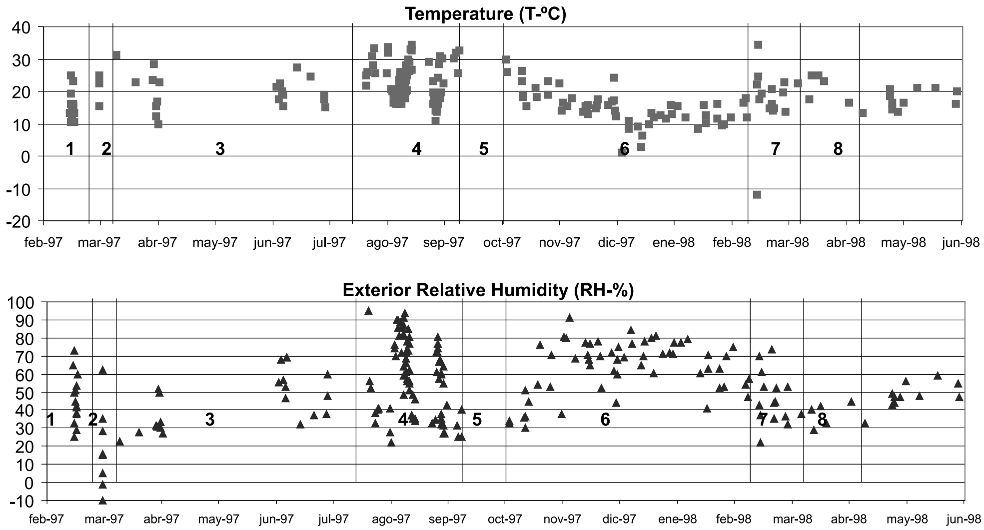

Fig. 10. Evolution of *T*/RH-EXT of the atmosphere in which the small specimen was held during the one year period of testing.

period (February 1997). Fig. 12 represents their evolution in more detail. Fig. 12 also contains the behaviour when the specimens were introduced in a fridge, (that will be commented later when describing period 2).

During this period of February 1997, a great change in *T*-EXT ($\Delta T = 17$–18°C) and in RH-EXT during day and night was registered. It is interesting to observe that the RH-IN (Fig. 2 right part) however changed very slightly, indicating that, the RH-IN remains apparently very stable in spite of the wide changes of *T*-EXT and RH-EXT.

Period 2: During this period, (first fortnight of March 1997) the specimens were introduced in a fridge in order to simulate an intense cooling period. It can be observed that immediately after been cooled below 0°C, the RH-IN increased to >80%, although it recovers the original values immediately after the temperature is raised again.

Period 3: During this period (3rd April 1997–August 1997) the specimens were sheltered from rain and day–night values were only seldom registered.

This period enables to identify the progressive evolution (drying) of the RH-IN following the increase in *T* typical of a summer in Mediterranean climates. Temperature reaches values above 30°C and the RH-IN falls to 40–45% during this period.

Period 4: At the end of the summer (September 1997) the specimens were exposed directly to the rain that occurred at that time. Two main features could be identified during this period, in which again relatively low temperatures were registered during night. The RH-IN increased during the direct exposure to rain, but fell down quickly afterwards. It seems like if the concrete is only superficially moistened and when the rain stops, it dries very quickly.

Period 5: In order to have an idea of the effect of high temperatures, before the summer was over, (end of September–beginning of October 1997) the specimens were artificially heated until 40°C in chambers having 30% RH. The total length of this period was about 30 days.

Period 6: During this period (October 1997–February 1998), the specimens were maintained sheltered from rain and measurements were made every week. As the temperature steadily decreases, the RH-IN again increases progressively.

An event of snow happened the 3rd December 1997. The *T*-EXT fell down to values below 0°C, which induced a sudden increase of RH-IN which reached 85%. However, as soon as the *T*-EXT increased, the RH-IN recovered again its previous values.

From October 1997, the weight was started to be measured simultaneously to the other measurements. It can be deduced that the increase in RH-IN from ≅30% (3 October 1997) to ≅70% (January 1998) induces an increase of 0.33% in relation to the dry weight of the specimen, and which represents a degree of saturation of 13.7%.

Period 7: In February 1998, the specimens were submitted to "artificial" rain (by means of immersion in water) in order to study the effect of different lengths of rain periods. In the figure the response when the specimen was submerged until full saturation is only shown. The total increase in *W* was of 2.41% in relation to the dry weight (40°C and 30% RH).

During the process of saturation, the RH-IN increased slowly and steadily. The sudden increase in RH-IN that was detected when the specimen was submitted to natural rain was not noticed. At the end of the saturation, when the weight reached a constant value, the

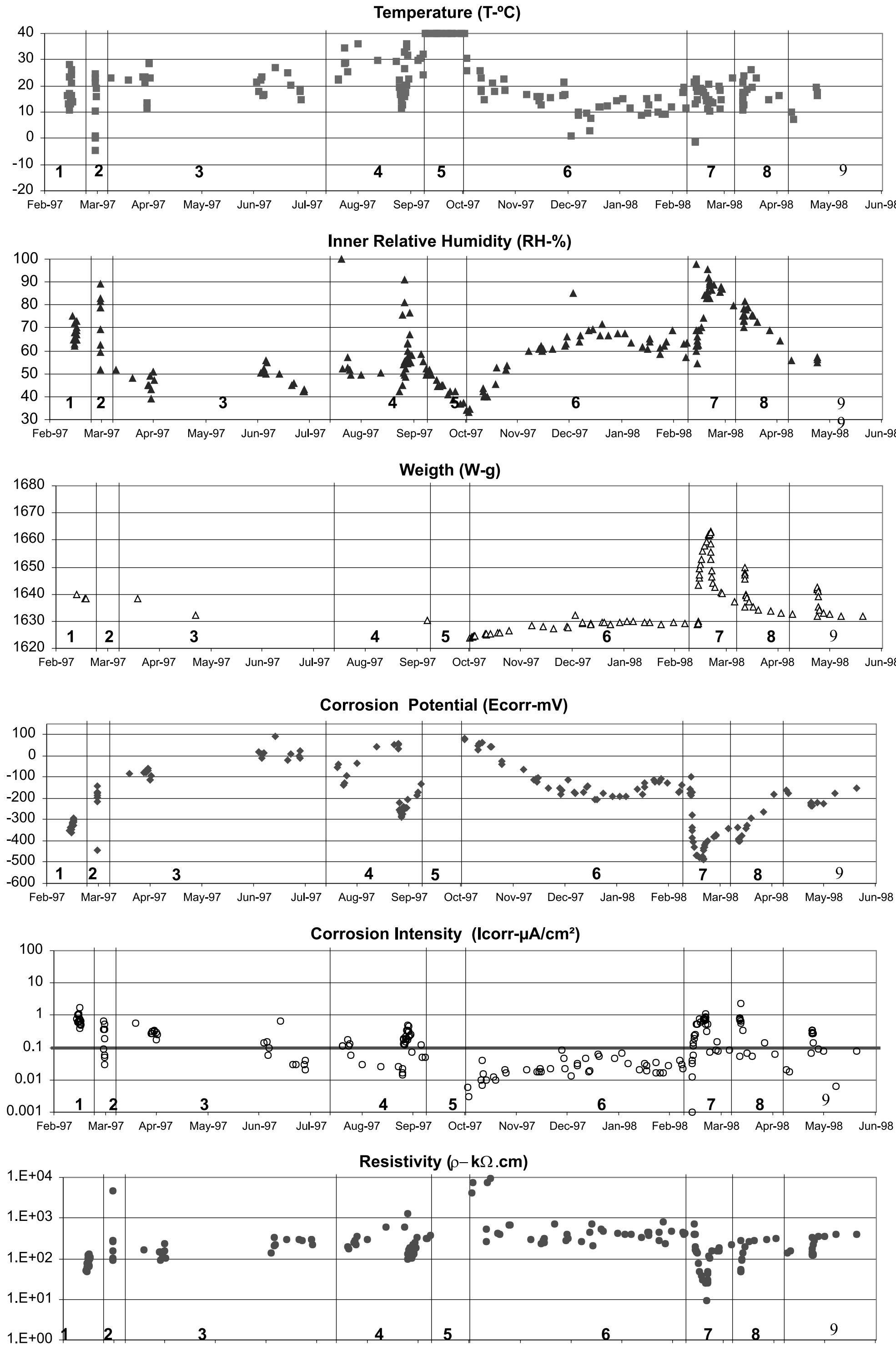

Fig. 11. Evolution of T-IN, RH-IN, Weight, E_{corr}, I_{corr} and resistivity of the small specimen during the same period than that shown in previous figure.

RH-IN was permanently at ≅93% RH. During subsequent drying, the RH-IN decreased slowly and progressively.

Also, during this period 7 an event of artificial freezing was studied. That is not reported here as it resulted similar to the previous one.

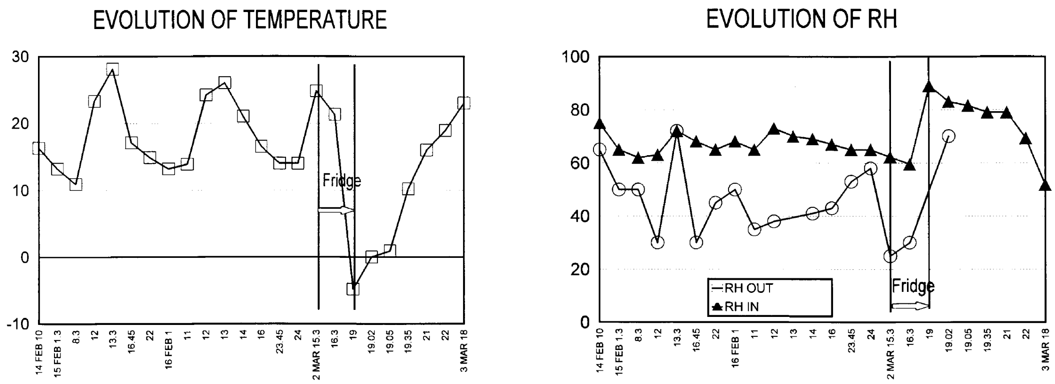

Fig. 12. A detail of the evolution of T/RH-IN during the day–night cycle and when introduced in a fridge at temperatures below 0°C.

Periods 8 and 9: Finally in March–April 1998, the specimens were artificially rewetted to simulate short rain periods (70 and 10 min). The water uptaken during these periods remained for many days.

Concerning the *corrosion performance* (period 1) of the bar embedded, the I_{corr} values registered at the beginning of the test (period 1) were high ($\cong 1$ $\mu A/cm^2$), with ρ values around 10 kΩ cm and relatively negative E_{corr} values (between −300 and −400 mV/SCE). The T daily cycles do influence these parameters by inducing parallel changes.

When the specimen is introduced in the fridge (period 2), the I_{corr} dramatically decreases in spite of the increase in RH-IN. The E_{corr} also lowers to more negative values and ρ increases.

At long term in sheltered conditions (periods 3, 4 or 6) it is interesting to notice that the specimen behaves as noncorroding because the I_{corr} values are lower than 0.1 $\mu A/cm^2$, the E_{corr} remain around 200 mV and the ρ lie in the range of 80–100 kΩ cm. Only when the concrete is wet (periods 7–9) the corrosion parameters indicate activity which means that only under the action of direct rain this specimen is developing corrosion.

4. Discussion

In order to understand the corrosion behaviour it has been necessary to study first how the weather (hydrothermal evolution) influences the concrete moisture. This has been feasible by monitoring the concrete weight changes. The interpretation of the behaviour has been made by using the following three basic laws: (a) the psicrometric abacus plots, (b) the graphs of moisture content RH-IN (those used for studying water isotherms) [9,10,14] and (c) the consideration of Kelvin's law expressing the relation between vapour partial pressure and maximum size of concrete pores filled with water [13].

A water isotherm of a concrete shows a hysteresis which indicates that, assuming equilibrium with the external atmosphere, there are two evaporable water, W_{evap}, contents giving the same RH-IN (those of the adsorption and desorption). Sellevold [10] has shown that samples drilled from in situ structures seem to have moisture contents of the desorption branch. However, until more information is obtained from outdoor structures, RH-IN should not be used to generally characterize the corrosion behaviour which depends on the W_{evap}.

Furthermore, the analysis of the results of present research has enabled the deduction that the continuous evolution of T induces a permanent nonstationary transfer of water (liquid and vapour) across the concrete and therefore, the RH-IN is not the expression of an equilibrium neither it indicates the maximum pore size filled with liquid water (Kelvin's law). If RH-IN does not represent an equilibrium, it cannot even be related to the two moisture (W_{evap}) contents, but with a set of them and in consequence, it cannot be used as the determining parameter of the corrosion behaviour.

In addition, in unsheltered conditions where rain feeds the concrete with liquid water, the RH-IN is a compromise between the vapour diffusion across the pore empty space and the progressive water uptaken by absorption.

In consequence, the corrosion rate has to be related not to the RH-IN but to the amount of liquid water, W_{evap}, as will be commented further.

4.1. Main features of weather influence

It is known that when T varies along day–night and seasonal cycles, the RH-EXT changes accordingly. However, the trend of RH-IN differs from the behaviour of the external atmosphere.

The main events that influence the concrete moisture may be grouped as follows:

1. The day–night cycles.
2. The seasonal cycles.
3. The extreme temperatures (below 5–10°C and above 25°C).
4. Rain periods.

Fig. 13 tries to summarize the consequences of the three first events in concretes sheltered from rain. Thus, in the left part of the figure, it has been plotted a W_{evap}/RH-IN graph (water isotherm) and in the right a psicrometric abacus.

The daily cycles induce negligible changes in the W_{evap}, due to the period it is too short to allow the bottom of the cavity (around 3–4 cm deep) to loose or gain moisture. Then, in the pore empty space, when T increases during day the water evaporates which makes the RH-IN to increase in spite of W_{evap} remaining almost unaltered. The opposite (condensation) happens when T decreases during night. The result is that day cycles only slightly make to change the RH-IN.

This trend is however reversed in the long-term (seasonal) behaviour. Periods 3 and 5 in Fig. 11 indicate that the RH-IN decreases as T increases due to the progressive release of water vapour outside the specimen and vice-versa.

The effect of extreme temperatures is also shown by the arrows in Fig. 13 (right part). Low T (below 5–10°C depending on the moisture content) induces an increase in RH-IN, not because water vapour is uptaken (in period 7 the specimen was introduced sealed in a fridge) but because the actual vapour content exceeds that of saturation at these low T. It is an "apparent" increase in RH-IN, because as soon as the T is raised, the RH-IN recovers previous (low) values.

At high T (arrows in the right part of Fig. 13) the behaviour is reversed and the RH-IN lowers indicating that the amount of vapour is very far from saturation, and the evaporation of the pore water into the pore empty space cannot compensate the vapour evaporating out of the concrete. In consequence the RH-IN drops and the amount of vapour in the pore space remain or lower depending on the T itself and of the length of the dry period. RH values as low as 25–30% may be recorded at the end of Madrid summer periods.

Rain completely changes the situation as it means the ingress of significant amounts of liquid water and vapour. Both penetrate simultaneously. After the rain period, part of the water evaporates and therefore the total amount of water uptaken depends on the previous moisture content and the length of the raining (not its intensity). The most important characteristic of the rain periods is not the amount of water but their length and frequency because each concrete has a maximum in its absorption ability. It is different with half of the year raining and half dry, than rain every two days. It has not been found in references in the literature on a systematic study of rain impact on concrete moisture, which however is very much needed, as it is the most important influencing parameter (likely with snowing) of concrete moisture in outdoor exposures.

4.2. Corrosion performance

As was mentioned the corrosion current, I_{corr}, cannot be related to RH-IN because this last parameter represents the vapour content in the empty pore space while corrosion develops under the action of liquid water and additionally, in natural weathering the amount of liquid water is not in equilibrium with the RH-IN. The same RH-IN in concrete figures several W_{evap} contents, and therefore, several I_{corr} values will develop.

Regarding the effect of temperature, the I_{corr} values do follow T trend as Figs. 8 and 11 have well illustrated.

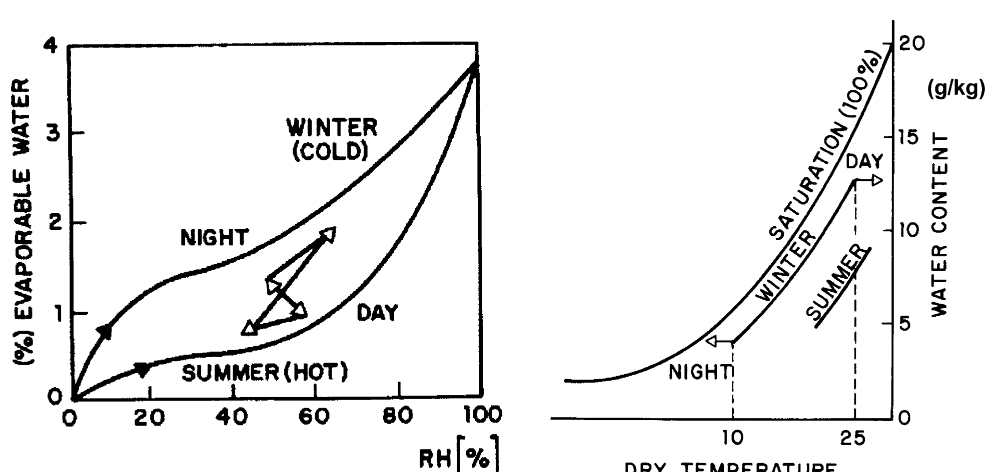

Fig. 13. Seasonal and daily evolution of T/RH-IN represented in two kinds of graphics: boundary water isotherms and psicrometric abacus.

However, a general relation to T (an Arrhenius behaviour) as that reported in [10] could not be found, because as its increase/decrease depends on other related parameters [15] that counter-balance the T tendency. Thus, an increase in T induces not only a decrease in resistivity, but a lowering of the oxygen content of the pore solution and a change in the pH and in the free chloride content, by changing the solubility of $Ca(OH)_2$ (it decreases when temperature increases) and of the chloride salts (they are more soluble when T increases). In consequence a general relation between T and I_{corr} could not be found, for instance, in the beam (Fig. 14).

The factor that has been found to fit better into the I_{corr} trend is the degree of water saturation, S_w, defined as the amount of liquid water (referred to 40°C and 30% RH) with respect to the capillary porosity in volume. Fig. 15 depicts the relation found in the concrete specimen. Below a certain S_w the I_{corr} is lower than 0.1 μA/cm^2 indicating that not enough pore connectivity exists to develop the corrosion process.

However, the most comprehensive parameter of the corrosion behaviour is the electrical resistivity, ρ. It shows a similar trend than the degree of saturation as has been reported [8,10] and is shown in Fig. 15. The I_{corr} relates as well to ρ, as was previously identified [16] by means of the expression $I_{corr}(\ \mu A/cm^2) = 10^4/\rho(\Omega\ cm)$. However, the ρ cannot encounter effects like that of the oxygen content, and in consequence, the corrosion has to be directly measured if calculation of the residual life or the propagation period of the corrosion, is looked for.

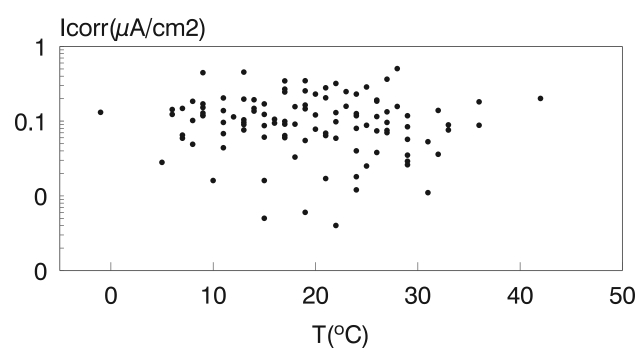

Fig. 14. Relation between I_{corr} and T in the beam.

5. Conclusions

Although some of the climate events have not been still thoroughly investigated and more research is needed to fully clarify the relation between weather and corrosion, the main conclusions that can be drawn from present study, are:

1. The corrosion rate (I_{corr}) values cannot relate to RH-IN, because this parameter, represents the vapour content in the pore space and, additionally, in natural weathering of concrete is the expression of a permanent nonstationary process of water and vapour transfer and therefore, RH-IN represents several degrees of saturation in evaporable water.
2. The T is the main driving force of the moisture content of concrete in sheltered from rain conditions, while rain periods (length and frequency) are responsible for the moisture content in unsheltered conditions.
3. The I_{corr} values neither univocally relate to the T because this parameter induces counter-balancing effects on several factors, among which the relevant, in present study, has been the content in liquid water, W_{evap}.
4. The moisture factor which better relates to the I_{corr} is the degree of capillary water saturation, S_w, (as defined in the text). However, the same S_w in different

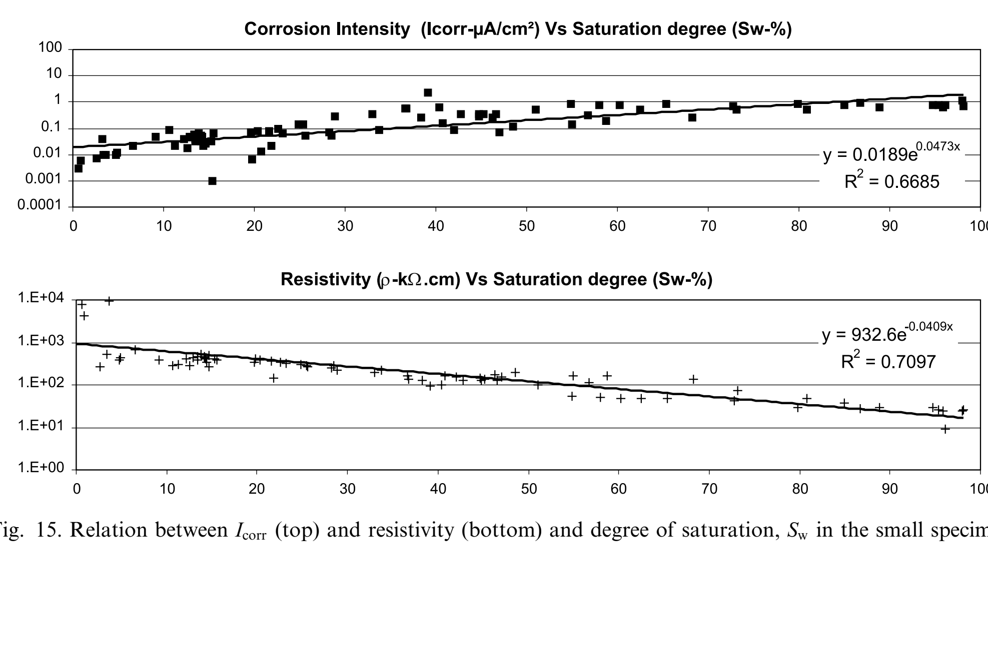

Fig. 15. Relation between I_{corr} (top) and resistivity (bottom) and degree of saturation, S_w in the small specimen.

concretes induce different I_{corr} values and therefore it cannot be taken as the most comprehensive parameter.

5. The most comprehensive one is the resistivity, although it still lacks encountering factors such as oxygen content in the pore liquid, or the amount of rust in the rebar, which however affect the I_{corr} values, and in consequence, the I_{corr} has to be directly evaluated if calculation of the corrosion propagation period is needed.

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