

Reinforcement corrosion in alkaline chloride media with reduced oxygen concentrations

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Abstract. It is commonly considered that the corrosion of steel in concrete is controlled by the oxygen content of the pore solution and there are service life models that relate the corrosion rate to the amount of oxygen. It is also commonly believed that in water-saturated conditions the oxygen content in the pores is negligible and that underwater there is no risk of depassivation and the corrosion rate is very low. However, the available data on corrosion rates in immersed conditions do not indicate such performance; on the contrary corrosion develops when sufficient chloride reaches the reinforcement. In the present paper, results are presented for tests performed in alkaline chloride solutions that were purged with nitrogen to reduce the oxygen content. The results indicate that at very low oxygen concentrations, corrosion may develop in the presence of chlorides. The presence or absence of corrosion is influenced by the amount of chloride, the corrosion potential and the steel surface condition.

1 Introduction

The cathodic corrosion reaction in concrete is believed to be the reduction of oxygen that penetrates through the concrete pores in the presence of water, according to the reaction [1]:



Owing to the high alkalinity of the pore solution, the steel bars embedded in concrete will remain passive unless a decrease of the pH of the electrolyte in contact with the metal occurs. This decrease can be induced by neutralization of the alkalinity by carbon dioxide (i.e. carbonation) or by the chlorides whose presence induce metal dissolution and further hydrolysis of the water by the metal ions, which are able to decrease the pH and result in the production of local corrosion and pits [2]. This type of corrosion is known to be detrimental to structural load-bearing capacity and as a consequence its prevention or reduction is very important. Several methods can be used to delay the onset of corrosion or to try to inhibit its development [3-5]. To suppress corrosion it is necessary to reduce the kinetics of the anodic and/or cathodic corrosion reactions. To inhibit the cathodic reaction, the removal of the cathodic reagents, namely water or oxygen, from the electrolyte is also an option. In the literature it is widely accepted that in water-saturated concrete the corrosion rate is controlled by oxygen diffusion through the concrete cover and thus aerobic corrosion cannot develop in the absence of oxygen. The present paper describes experiments that were carried out in solutions simulating those contained within concrete pores, with several different concentrations of chloride. By bubbling nitrogen the dissolved oxygen content was reduced, although less than 1 ppm remained

due to the possible impurities in the nitrogen gas. Interesting results were obtained when measuring corrosion in these conditions, demonstrating that it is possible to have active corrosion due to chloride attack even when the oxygen concentration in the electrolyte is reduced. In these conditions, the presence or absence of corrosion and its morphology depends on the concentration of chloride in contact with the steel, its corrosion potential and the surface roughness of the steel.

2 Experimental

The experiments simulated both freely corroding and cathodic protection conditions and therefore the experiments were carried out at both the free corrosion potential and controlled potentials.

2.1 Corrosion cell preparation

Due to very alkaline solutions, polyethylene corrosion cells (250 ml capacity) were used in all the experiments. Simulated concrete pore solutions (saturated $\text{Ca}(\text{OH})_2$) were prepared using demineralized water that had been decarbonated by boiling. A range of different concentrations of chloride were used in the experiments. The cell designs for progressive chloride addition and fixed chloride concentration tests are shown in Figure 1. Nitrogen was continuously bubbled for the whole duration of the experiments to reduce the oxygen concentration. The chloride addition was made with a pipette. In the case of free corrosion potential experiments (Figure 1(a)), three identical electrodes were tested, while in the case of potentiostatic tests, only one electrode was present in each cell (Figure 1(b)).

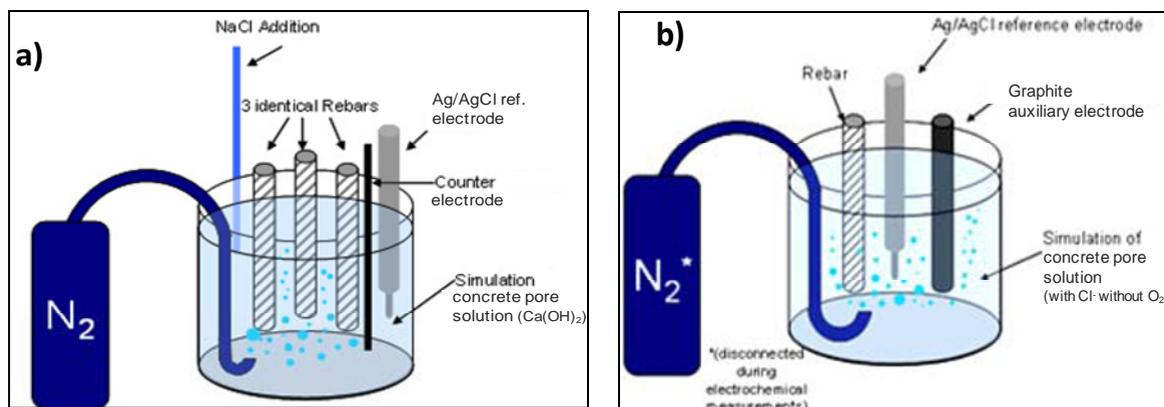


Fig 1. Cell scheme used for free and controlled corrosion potential tests. a) Free corrosion potential: Progressive chloride addition. b) Free and controlled corrosion potential: Fixed chloride concentration.

2.2 Test procedures

Free corrosion potential and controlled corrosion potential experiments were made. An Ag/AgCl electrode was used as the reference in all tests and all potentials quoted are with respect to this reference electrode. At the free corrosion potential the chloride concentration was either increased progressively (by adding aliquots with a pipette until concentrations of 2.5M in NaCl were achieved, see Figure 2) over the course of the test or it was fixed from the beginning, whereas under potentiostatic conditions, the chloride concentrations (Figure 2) were always fixed from the beginning of the test.

2.2.1 Free potential corrosion test: progressive chloride addition

Three steel bars were introduced into a cell containing saturated $\text{Ca}(\text{OH})_2$ solution (Figure 1a). The steel area exposed to the electrolyte was 3.77 cm^2 . After 24 hours of N_2 bubbling, the O_2 concentration in the solution was checked and the value was found to be around 0.4 ppm. At this moment, a progressive addition of 6M NaCl to the cell was started (at a rate of 1 ml every 30 minutes). The test was stopped when the chloride concentration in the cell reached the value of 2.5M and the steel exhibited a corrosion current density, I_{corr} , $>0.2 \mu\text{A}/\text{cm}^2$, which indicates steel depassivation. The total duration of the experiment was approximately 130 hours with continuous displacement of the O_2 by bubbling N_2 through the solution. The electrochemical parameters measured during the test were the corrosion potential and the corrosion rate, I_{corr} , of the three steel bars. The corrosion rate was measured by means of the polarization resistance technique using a B value of 26 or 52 mV depending on whether the steel was active or passive respectively [6]. The oxygen concentration in the solution was measured at different time intervals from the beginning of the test, using an oxygen meter with an ORION electrode. The pH values were measured over the course of the test by means of an electrode designed for very high alkalinities and an ORION 5STAR pH meter.

2.2.2 Free potential corrosion test: fixed chloride concentration

In this type of test, the chloride concentration was fixed from the beginning. The cells used were of the design shown in Figure 1b. Two chloride concentrations were chosen for short-term experiments and for comparison between electrochemical and gravimetric results, specifically 0.5M and 2.5M NaCl. The experimental procedure was the same in both cases except that the 2.5M NaCl experiments lasted for five days and the 0.5M NaCl experiments lasted for one month; corrosion potential (E_{corr}) and corrosion rate (I_{corr}) were recorded.

2.2.3 Free corrosion test: solution without chlorides

A highly alkaline solution (0.3M KOH + $\text{Ca}(\text{OH})_2$ sat, pH=13.4) was prepared. Chloride was not added to the solution and the oxygen was reduced (to around 0.5 ppm) by N_2 bubbling for 24h. Corrosion potential and corrosion rate were measured over the 20 days of the test.

2.2.4 Potentiostatic test

In these experiments the chloride concentration was fixed from the beginning. A potentiostat was used to control the potential of the steel (working electrode). Short-term experiments (24h) were made using saturated $\text{Ca}(\text{OH})_2$ solution with additions of 0.1M, 0.5M and 2.5M NaCl at potentials of -850mV, -650mV, -550mV and -350mV. Subsequently, a longer test of around 30 days was conducted using a 2.5M NaCl solution and polarizing the steel at potential values of -540mV, -450mV, -477mV and -350mV. I_{corr} values (measured using the polarization resistance method) and E_{corr} were measured at the beginning and end of the tests, before and after switching off the potentiostat. The current flowing between the steel and the counter electrode during potentiostatic polarisation was logged over the course of the test. The electrochemical weight losses (i.e. the metal mass loss due to the current passing under potential control) were calculated from the integral of the anodic current curve, in order to compare the results with the mass losses obtained gravimetrically.

2.3 Electrochemical techniques

2.3.1 Corrosion potential measurement

The corrosion potential values were monitored using an AGILENT 34970A datalogger, which measured the potential difference between the steel and the Ag/AgCl reference electrode.

2.3.2 Corrosion rate measurement

A potentiostat (AMEL 550) with ohmic drop compensation was used. The polarisation resistance value, R_p , was measured by linear polarization over a range of ± 10 mV centred on the E_{corr} and with a scan rate 10 mV/min. The corrosion current, I_{corr} , was calculated by dividing the Stern-Geary constant B (26 mV) by the R_p value.

For potentiostatic tests the potentiostat used was an AMEL 550. The current flowing between the steel and the counter electrode was monitored during the tests using an AGILENT 34970A datalogger.

3 Results

3.1 Free potential corrosion test: progressive chloride addition

Figure 2 shows the average value of the corrosion potential and the corrosion rate of the three bars (which exhibited very similar individual values) after each chloride addition to nitrogen-purged $\text{Ca}(\text{OH})_2$ solution. Figure 2 also shows the pH of the solution. It can be seen that the potential evolved towards more negative values during the progressive increase in the chloride concentration in the electrolyte. The initial potential of the steels was around -350 mV, but fell to -570 mV when the NaCl concentration in the electrolyte was 2.5M. The trend however was not continuous as the potential dropped to values around -570mV with small addition of chlorides and then shifted to values around -470mV before returning to -570mV.

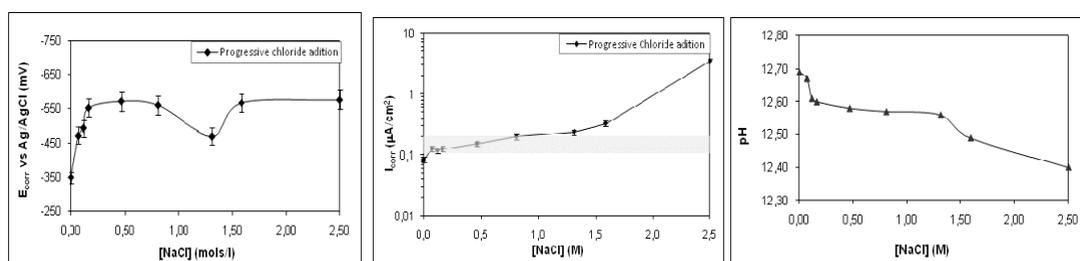


Fig 2. Left: Corrosion potential (versus Ag/AgCl electrode). Centre: Corrosion rate measured during experiment with progressive chloride addition to nitrogen-purged $\text{Ca}(\text{OH})_2$ solution. The grey area in the central figure marks the assumed boundary between the passive corrosion state and the active corrosion state. Right: pH value during the experiment.

The central part of Figure 2 shows the corrosion rate, I_{corr} , whose initial values were around $0.08 \mu\text{A}/\text{cm}^2$ in the absence of chloride. As the chloride concentration was increased, the I_{corr} progressively increased and its value reached the threshold value between $0.1 - 0.2 \mu\text{A}/\text{cm}^2$, which is shown as a grey band in the figure, and is the commonly assumed boundary value between passivity and active corrosion [6,8]. The I_{corr} value remained in this boundary region until the chloride

concentration was increased to around 0.8M. When the chloride concentration was higher than 0.9M the I_{corr} value exceeded $0.2 \mu\text{A}/\text{cm}^2$. The highest I_{corr} value recorded was $3.5 \mu\text{A}/\text{cm}^2$ in the solution containing 2.5M NaCl.

The evolution of the pH with NaCl addition is shown at the right hand side of Figure 2. There was a sharp initial decrease in pH at about 0.25M chloride concentration. Between 0.20M and 1.5M the pH value remained fairly constant. About 1.5M the pH again decreased until reaching a value of 12.4 at the end of the experiment. The reasons for the change in pH value were not explored because they were not essential for the sake of the experimentation. One of the reasons might be that corrosion induces the acidification due to the hydrolysis of the water molecules by metal ions.

3.2 Free potential corrosion test: fixed chloride concentration

Longer tests in $\text{Ca}(\text{OH})_2$ plus 2.5M and 0.5M NaCl solutions with N_2 bubbling continuously, were also performed. Figure 3 shows the mean corrosion potential of six steel bars immersed in 2.5M NaCl (this solution was made by duplicate) for five days and the mean corrosion potential of three bars immersed in 0.5M NaCl solution for one month. In both cases, the corrosion potential value decreased with time. The initial potential value was around -500mV for the steel immersed in 2.5M NaCl solution and -470mV for the steel in 0.5M, with more fluctuations observed in the 2.5M NaCl solution.

The evolution of the corrosion rate is also shown in Figure 3. The corrosion rate values for the 2.5M and 0.5M NaCl curves are an average of six steel electrodes (two cells) and three steel electrodes (one cell), respectively. The same trend for the E_{corr} value was found for both chloride concentrations. From the beginning of the test, the I_{corr} value was high: $2.33 \mu\text{A}/\text{cm}^2$ and $1.06 \mu\text{A}/\text{cm}^2$ for 2.5M and 0.5M NaCl solution, respectively. I_{corr} values increased continuously with time of immersion until reaching values of $4.3 \mu\text{A}/\text{cm}^2$ for the 2.5M and 0.5M NaCl solution, respectively. By applying Faraday's law it is possible to calculate the expected weight loss [6]. A comparison of this "electrochemical" weight loss and the real gravimetric losses is shown in the right hand side of Figure 3. All values show a good agreement between the measured and predicted weight losses. Only three steel rods in the 2.5M solution exhibited weight losses that did not lie in the range of "two times accuracy" [6] of the linear polarization technique (see parallel lines in Figure 3 right), but the mean value does.

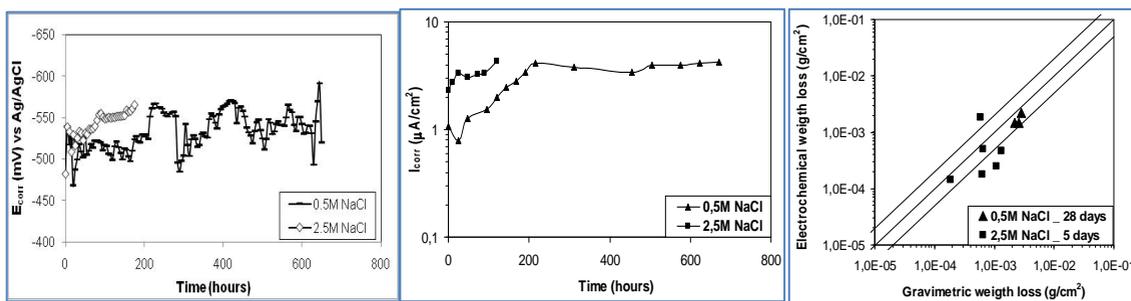


Fig 3. Left: Corrosion potential, centre: corrosion rate evolution and Right: weight loss results for the steels immersed in 2.5M and 0.5M NaCl nitrogen-purged $\text{Ca}(\text{OH})_2$ solutions.

Despite the high values of corrosion rate measured, visual observation of the test specimens at the end of the test in 2.5M chloride only showed areas with corrosion staining and very small pits. Figure 4 shows some pictures of one of the steel electrodes tested for 5 days in the 2.5M NaCl nitrogen-purged $\text{Ca}(\text{OH})_2$ solution at the free corrosion potential. The oxides were more visible in the 0.5M NaCl solution test that lasted one month. Figure 4 shows some pictures of one of the steels

tested in these conditions. It can be seen that corrosion products were formed in a line along the bar which may be formed during the bar fabrication. Crevice corrosion was also observed at the edge of the tape used to delimit the working area. In both cases (0.5M and 2.5M NaCl solutions) the corrosion occurred only in areas with surface imperfections such as seams or rolled laps. Both the metallurgical defects and the interface with the tape used to delimit the working area, served as sites for corrosion initiation. These imperfections seem to be the preferential sites for pit initiation and the border of the tape for crevice corrosion. It seems that the high values of I_{corr} are truly indicative of active corrosion despite the fact that the oxides were not visible to the eye until a certain amount was formed (they were more visible in the longer duration experiment).

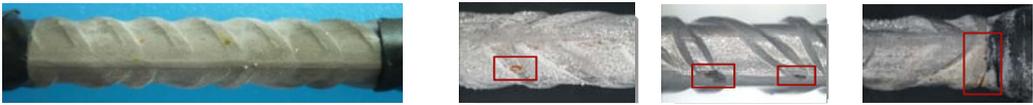


Fig 4. Appearance of the steel immersed during 5 (left) and 30 (centre and right) days in 2.5M NaCl solution.

Regarding the fact that the I_{corr} values in the 0.5M alkaline solution in the present fixed-chloride concentration tests (Figure 3 centre) were higher than in the test with increasing chloride additions (Figure 2 centre), this behaviour was attributed to the nucleation time; that is, in the tests with the increasing chloride concentration the time between additions was shorter than the exposure time in the fixed chloride concentration tests. These experiments were performed to check whether the pits are immediately nucleated or whether they need an induction period before becoming active. It seems therefore that nucleation time is another parameter influencing the values of I_{corr} recorded.

3.3 Free corrosion test: solution without chlorides

Corrosion potential and corrosion rate evolution data for the steel in contact with a highly alkaline solution without chlorides are shown in Figure 5. This experiment was performed in order to determine how the corrosion parameters evolve in alkaline solutions without chlorides. Despite the low oxygen concentration (<0.5 ppm) measured in the solution, the corrosion potential was in the cathodic region only for the first few days and it evolved towards more noble values with time, reaching values that were more anodic than -200 mV. The highest value of I_{corr} occurred during the first days of the test. Later, the corrosion rate values decreased with time, reaching very small values and following the same trend as E_{corr} towards passivity values. Moreover, no visual evidence of damage or corrosion was observed on the steel after 20 days' exposure.

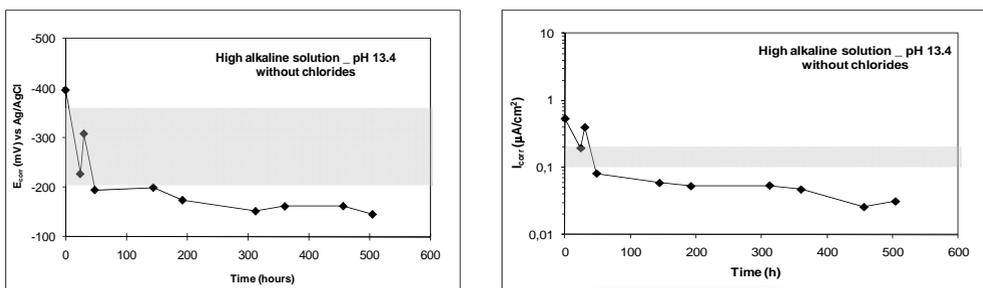


Fig 5. Corrosion potential and corrosion rate evolution for the steel immersed in a very high alkaline solution without chlorides with continuous bubbling of nitrogen.

3.4 Potentiostatic test: short term test

Figure 6 shows the evolution of the current flowing between the steel and the counter electrode (CE, graphite) for the potentials applied. The currents were anodic in all the solutions at -350mV, while at -650mV and -850mV they were cathodic. At -550mV the greatest cathodic current was for 2.5M

NaCl. Figure 6(c) shows that a potential value of -550mV was not enough to protect the steels immersed in 0.1M and 0.5M NaCl solutions. At these concentrations the currents changed constantly from anodic values to cathodic values. However, the current flowing between the steel immersed in 2.5M NaCl and the CE was always cathodic and the steel was therefore protected. This is the opposite situation to that which could have been expected, as in freely corroding conditions the 2.5M solution would be expected to be the most aggressive.

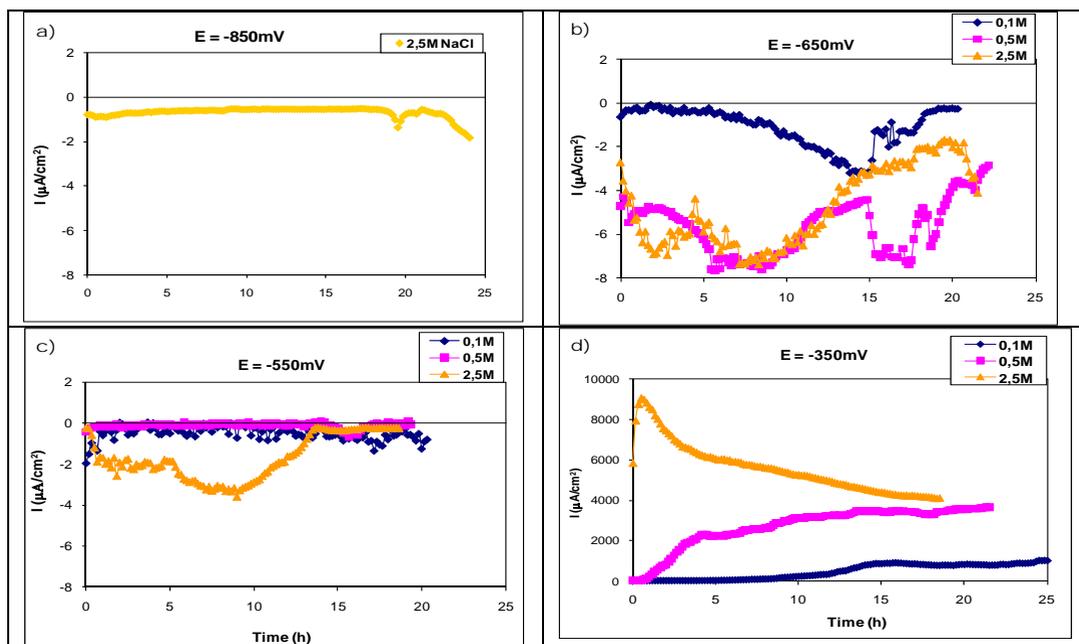


Fig 6. Potentiostatic tests. Current variation with time. Steels immersed in different chlorides concentration solutions for different set potential values: a) $E=-850\text{mV}$, b) $E=-650\text{mV}$, c) $E=-550\text{mV}$ and d) $E=-350\text{mV}$

The weight loss was calculated by applying Faraday's law, using the integral of the anodic current curve. Although not given in present work the values of these weight losses calculated from the electrochemical results show a good agreement with the gravimetric data. Anodic currents (due to iron oxidation) were only detected in the experiments where the potential was fixed at -350 mV. Working at other potentials always gave rise to cathodic currents. For this reason, only the steels tested at -350mV should be taken into account when comparing mass losses obtained gravimetrically and electrochemically. The appearances of the steels tested at several conditions are summarized in Figure 7.

At the most negative potentials (-850 mV and -650 mV) no signs of corrosion were found. Similarly, the steel immersed in 2.5M NaCl and polarized at -550mV did not show any corrosion products. However, some corrosion pits and slight corrosion products were formed on the steels immersed in 0.1M and 0.5M NaCl at a potential of -550mV. When the potential was set at a higher value (-350mV), voluminous oxides were generated for all the chloride concentrations tested. In this condition, the amount of oxides produced increased with chloride concentration although the oxide was more voluminous but also more localized in a 0.5M solution.

SET POTENTIAL VALUE	CHLORIDE CONCENTRATION		
	0.1 M	0.5 M	2.5 M
-850mV	Not tested	Not tested	
-650mV			
-550mV			
-350mV			

Fig 7. Appearance of the steels immersed at 0.1M, 0.5M and 2.5M NaCl solution and polarized at -850mV, -650mV, -550mV and -350mV for a 1 day of exposure.

3.5 Potentiostatic test: long-term test

In order to establish the protection potential more accurately a long-term potentiostatic test was performed in $\text{Ca}(\text{OH})_2 + 2.5\text{M NaCl}$ solution. Four steels were tested at potential values of -540, -477, -450 and -350 mV. Anodic currents were recorded when the bars were controlled at -350, -450 and -477 mV. The current values increased with the time of immersion, indicating an apparent active state. However, fluctuating anodic and cathodic currents were recorded when the bar was controlled at -540mV. This bar exhibited a decrease in current with time in comparison with the initial value. It seems that in the tests the corrosion threshold potential for 2.5M solution was -540mV, while, for the other more dilute solutions the potential was more cathodic than -540mV. It was observed that the corrosion rate decreased with a decreasing control potential value, which confirms the results found in previous tests, namely that the bars that were corroded at more negative potentials (-540mV), had less corrosion than the bars corroded at more positive potentials (-350mV).

4 Discussion

There are four main aspects of the results to discuss:

- 1) the influence of the oxygen concentration on active corrosion and the ability of additional cathodic reactions, such as the decomposition of water, to develop,
- 2) the role of the potential, which is clearly illustrated in the results, because corrosion only takes place above a certain threshold potential,
- 3) the chloride concentration and
- 4) the role of the steel surface imperfections or defects, which has been identified as being more important than thought in the past.

The relative importance in the electrolytes simulating the concrete pore solution of the four aspects needs further research to be fully elucidated.

The results show that active corrosion can develop in solutions with low oxygen contents. The oxygen concentration is not then, the main controlling factor for developing corrosion and its diffusion through the concrete cover is not the only determining parameter for the kinetics of corrosion. For active corrosion the presence of chlorides is required, but the critical chloride

concentration is also related to the existence of defects in the steel surface. That is, surface defects and chloride concentration are the main parameters controlling active corrosion in a reduced oxygen environment. The values of corrosion rate can reach quite high values.

Concerning the places where pits and oxides nucleate, steel reinforcement contains many surface imperfections, since they are corrugated bars whose diameter is reduced during fabrication by hot-drawing, leading to the formation of longitudinal bends that contain microscopic defects or small holes in which differential aeration can develop, for example at the border of the adhesive tape used in the present experiments. Also the corrugation induces areas with different roughness. All these factors seem to play an important role in the initiation and development of active corrosion areas.

5 Conclusions

It is a generally assumed statement that the presence of very low concentrations of oxygen in chloride solutions is a guarantee of the absence of corrosion. However, the results reported above provide contrary evidence. It is possible to have active corrosion due to chloride attack, even when the oxygen concentration in the electrolyte is reduced. The presence or absence of corrosion is influenced by the amount of chloride and the surface roughness. Pits nucleate at metallurgical defects and at the border of tape used to delimit the working area. These imperfections seem to be preferential sites for pit initiation and the border of the tape for crevice corrosion.

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6 References

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