

Inhibiting behavior of nitrites in corrosion of reinforcing steel in basic solutions simulating the electrolytic environments of micropores concrete in the initiation period

P. Garcés & E. Zornoza

Dept. Ingeniería de la Construcción. Universidad de Alicante (Spain)

P. Saura

Dept. Construcciones Arquitectónicas. Universidad de Alicante (Spain)

C. Andrade

Instituto Eduardo Torroja de Ciencias de la Construcción, Madrid (Spain)

ABSTRACT: Measurements of the corrosion rate of corrugated steel bars have been carried out in solutions simulating electrolytic chloride environments in the micropores of concrete in the initiation period. It has been studied the effect of sodium nitrite as a corrosion inhibitor when added to the mentioned solutions. The solutions for the experiments were prepared by addition of different volumes of FeCl_2 0.2 M into a saturated solution of calcium hydroxide until the target pH was reached in each case. This is the soluble compound produced during the corrosion of steel as a result of chloride attack. It has been observed a significant improvement in using nitrite as inhibiting agent in these systems, but its efficiency decreases when the pH is reduced. The corrosion seems to be related to the $[\text{Cl}^-]/[\text{OH}^-]$ ratio in three different regions of pH identified from acid to alkaline pH values.

1 INTRODUCTION

Steel embedded in concrete passivates due to the alkaline nature of the concrete pore solution (Page & Treadaway 1982). Reinforcement corrosion develops when the alkalinity is neutralized. One of the main causes of localized attack is the penetration of chloride ions through the porous reinforcement cover (Alvarez & Galvele 1994, Gorda 1970, Hoar 1967, Janik-Czachor et al. 1975). These ions need a certain critical concentration to induce corrosion. This threshold depends on several factors, one of which being the nature of the accompanying cation (Andrade & Page 1986). Once chlorides have depassivated locally the steel surface, corrosion pittings are usually observed. The pitting corrosion mechanism implies a progressive acidification of the solution inside the pits due to the increasing presence of Fe^{2+} , therefore the corrosion rate increases because of the lower pH value.

In a previous work (Garcés et al. 2005) it was studied the corrosion of construction steel immersed in simulated concrete pore solutions during its progressive acidification due to the presence of increasing amounts of FeCl_2 generated by active corrosion or due to the presence of NaCl (sea water). The concrete pore solution was basically composed of saturated $\text{Ca}(\text{OH})_2$. These basic solutions are first neutralized at the steel surface during active corrosion and then reach an acid pH value due to the generation of Fe^{+2} ions. In general, three regions in the corrosion current I_{corr} vs. pH diagram can be identified: (a) an acid region extending from pH=0 to around 4.5-5, (b) a neutral region extending from 4.5-5 to 9-9.5 and (c) a basic region for pH values above 9-9.5. The general trend is S-shaped as function of pH value. In the acid region I_{corr} steeply decreases as pH increases. In the neutral region I_{corr} becomes almost independent of the pH value and in the basic region I_{corr} again decreases with increasing pH. This trend is rather general, although for a particular case, it depends on several other variables such as: oxygen concentration, anion type, stirring of the electrolyte, temperature, type of steel, etc.

It is widely known the inhibiting effect of nitrites on the corrosion rate of steel embedded in concrete (Batis et al. 1996, Garcés et al. 2008, Page et al. 2000). Nitrites has shown a perfect compatibility with concrete and it is noticeable its relative low cost as well as its effectiveness in chloride-contaminated (Lundquist et al. 1979, Sideris & Savva 2005) and carbonated (Anstice 2005) concretes, but in the revised

literature it has not found the behavior of sodium nitrite and its efficiency to reduce corrosion levels at the initial stage of the corrosion process due to a chloride-contamination process in the concrete.

In the present paper several solutions, simulating the conditions occurring at the steel surface generated by chloride attack, have been prepared with and without nitrites. The results have been analysed in different ways in order to reach a better understanding of the role of nitrite and the $[Cl^-]/[OH^-]$ ratio on the depassivation threshold and on the kinetic aspects of the corrosion process of the metal/electrolyte system. Polarization resistance and electrochemical impedance spectroscopy have been used as measuring techniques (Andrade & González 1978, Keddad et al. 1981, Whitman et al. 1983).

2 EXPERIMENTAL DESCRIPTION

2.1 Materials and solutions

Corrugated steel bars were used for the experiments. The exposed area of the bars was 12.04 cm^2 . Previous to the experiment the bars were cleaned in $HCl:H_2O$ 1:1 with hexametylenetetramine solutions, abraded with abrasive paper and degreased in acetone. Adhesive tape was used for limiting the active area.

The corrosion cell was similar to that used in previous studies (Andrade & González 1978, Garcés et al. 2008). Two identical steel bars and a carbon auxiliary electrode were immersed in each cell. The I_{corr} results are always the average of the two bars immersed in the cell.

A range of solutions simulating the pore solution evolution during the corrosion initiation period has been prepared. Table 1 shows the solutions studied. It gives the values of initial pH and conductivities of the different solutions prepared. The solutions for the experiments were prepared by addition of different volumes of $FeCl_2$ 0.2 M into a saturated solution of calcium hydroxide until the target pH was reached in each case. These solutions would simulate the progressive acidification that takes place during the corrosion initiation period due to the release of Fe^{+2} ions, which reacts with H_2O to yield $Fe(OH)_2$ and H^+ . Four sets of these solutions were prepared: (a) without nitrites; (b) with 0.1 M $NaNO_2$; with 0.5 M $NaNO_2$, and; (d) with 0.1 M $NaNO_2$ during 1 week and then $NaNO_2$ was added until 0.5 M was reached.

Table 1. Characterization of synthetic solutions. The solutions for the experiments were prepared by addition of different volumes of $FeCl_2$ 0.2 M into a saturated solution of calcium hydroxide until the target pH was reached in each case.

Solution Target pH	$[NaNO_2]$ (M)	Initial pH	Final pH	Final Conductivity	Mean I_{corr} ($\mu A/cm^2$)
$Ca(OH)_2$ sat.	-	12.41	12.61	7.90	3.00
pH 11	-	11.07	10.98	4.26	12.46
	0.1	11.13	10.96	13.59	3.09
	0.5	11.06	10.87	50.80	2.40
pH 10	-	10.07	10.02	3.98	12.77
	0.1	10.02	9.58	13.43	2.08
	0.5	9.98	9.22	46.10	1.24
pH 9	-	8.87	8.96	4.14	10.89
	0.1	8.45	10.62	13.29	1.93
	0.5	8.24	9.09	45.70	2.53
pH 8	-	8.02	7.88	4.73	17.84
	0.1	6.62	8.71	13.52	1.97
	0.5	6.57	5.63	45.50	8.49
pH 7	-	6.87	6.85	11.68	23.53
	0.1	4.65	3.59	15.37	83.02
	0.5	5.44	5.34	43.90	14.93

The conductivity and the pH of the solutions were measured several times during and at the end of each test. A Crison model 2002 ion analyser microprocessor pH-meter and a combined electrode for the pH

range 0-14 were used to measure pHs. Conductivity measurements were taken from a conductimeter Crison model 525.

2.2 Measurements techniques

The electrochemical technique used to measure the corrosion rate was the Polarization Resistance method (R_p) (Barnartt 1971, Stern & Roth 1957).

The R_p is the slope of the polarization curve around the corrosion potential: $R_p = \Delta E / \Delta I$ when $\Delta E \rightarrow 0$. The R_p value is related to I_{corr} by means of a constant, denominated B by Stern (Stern & Roth 1957). It was stated by Stern (Stern & Roth 1957) that when using a mean B value of 26 mV, the maximum I_{corr} error factor is 2. For the case of steel embedded in concrete, a value of 26 mV was found (Andrade & Alonso 1996) for the active state (corrosion) whereas $B=52$ mV is more appropriate for passive steel.

R_p and corrosion potential were periodically measured during the time of the experiment. The reported results are the average of two identical bars. In order to validate the electrochemical I_{corr} values obtained through R_p measurements, they were compared by means of Faraday's law to the gravimetric losses obtained in the same rebars. In the results obtained, the Mean I_{corr} was also used as a corrosion rate indicator. The values were obtained by dividing the area of the I_{corr} plots (integration of the I_{corr} -time curves) by the duration time of each test expressed in days. The quantity, Mean I_{corr} , has the units of $\mu A/cm^2$ and represents the averaged I_{corr} value in the testing period.

3 RESULTS

Table 1 shows the initial pH values of solutions with different concentrations of $NaNO_2$. It can be observed in this table that the addition of $NaNO_2$ does not affect the initial pH for solution with high initial pH, when the passive layer is very stable. At pH 9 it can be noted that sodium nitrite produces a slight decrease in pH. Moreover, for solutions with pH 8 and 7, the addition of sodium nitrite reduces significantly the pH of the solutions. Thus, the influence of sodium nitrite on the pH of the solution may be related to the presence of Fe^{+2} and the pH itself as it will be discussed below in next section.

In Figure 1, the evolution of I_{corr} and E_{corr} with time of steels submerged in solutions of initial pH 11 without sodium nitrite and with 0.1 M and 0.5 M of $NaNO_2$ is presented. It can be observed that the addition of sodium nitrite produces a reduction of the corrosion rate. The increase of the inhibitor concentration implies an improvement in the inhibiting effect at the end of the experiment. On the other hand, the presence of sodium nitrite produces a shift of E_{corr} towards more noble values respect to the solution without sodium nitrite, supporting the reduction of the corrosion rate that was registered. The evolution of I_{corr} and E_{corr} registered for steels in solution of pH from 10 to 8 was rather similar to that shown in Figure 1.

It can be observed that the addition of sodium nitrite produces a reduction of the corrosion rate. The increase of the inhibitor concentration implies an improvement in the inhibiting effect at the end of the experiment. On the other hand, the presence of sodium nitrite produces a shift of E_{corr} towards more noble values respect to the solution without sodium nitrite, supporting the reduction of the corrosion rate that was registered.

Figure 2 shows the evolution of I_{corr} and E_{corr} with time of steels submerged in solutions of initial pH 7 without sodium nitrite and with 0.1 M and 0.5 M of $NaNO_2$. At this pH, sodium nitrite in concentration of 0.1 M produces a slight decrease in the corrosion rate but, the addition of sodium nitrite in higher concentration does not reduce corrosion level, showing an evolution almost identical to the steels of the solution without sodium nitrite. This behaviour is clearly supported by the corrosion potential, where it can be noted that on solution with 0.1 M of sodium nitrite presents its corrosion potential shifted towards more positive values.

In Figure 3, the evolution of I_{corr} and E_{corr} with time of steels submerged in solutions of different initial pH is plotted. In this set I_{corr} and E_{corr} are presented for 28 days in the first part of the graph. After this, sodium nitrite was added up to 0.1 M and 9 days after it was increased up to 0.5 M while I_{corr} and E_{corr} was being registered. In the second step, the addition of 0.1 M of sodium nitrite produces a slight decrease in I_{corr} in steels submerged in all the solutions at any pH but steels of solution of pH 7 remains unchanged. The inhibition effect of this addition is also observed in E_{corr} values, since it can be noted that E_{corr} progressively shifts to more positive values with two exceptions: steels of saturated solution of calcium hydroxide and those of pH 7 are not affected by this addition of sodium nitrite. In the first case it is due to steels are

perfectly passivated and in the second one it seems that the quantity of sodium nitrite is not enough to produce any changes on the steel condition. In the third step, the increase in sodium nitrite up to 0.5 M does not affect I_{corr} values of none of steels but those submerged in solution of pH 7 where it can be observed a minor decrease of this parameter. This little change is also accompanied by an expected increase in E_{corr} .

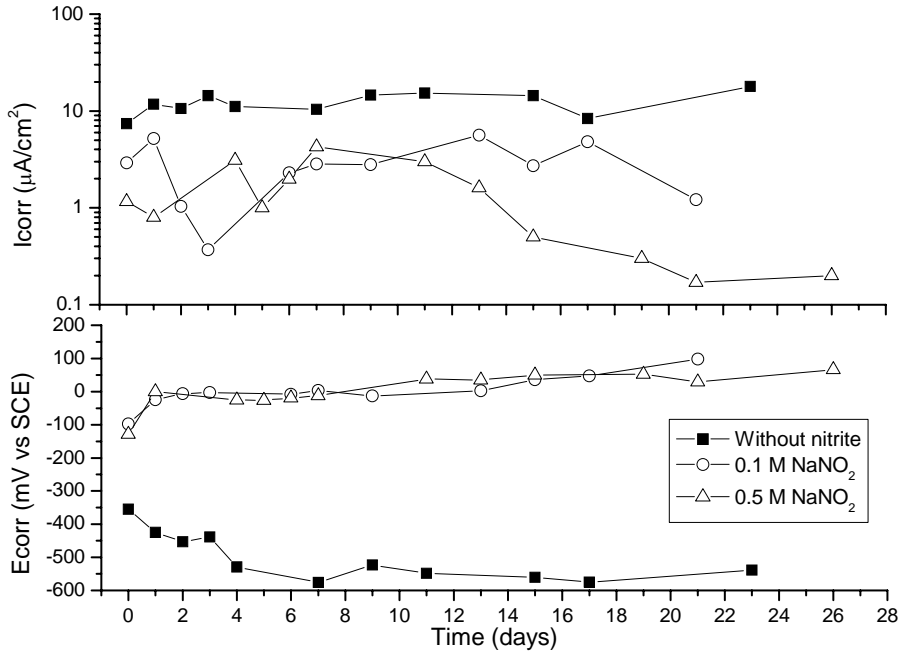


Figure 1. Evolution of I_{corr} and E_{corr} vs time in solutions of initial pH 11 with different concentration of sodium nitrite.

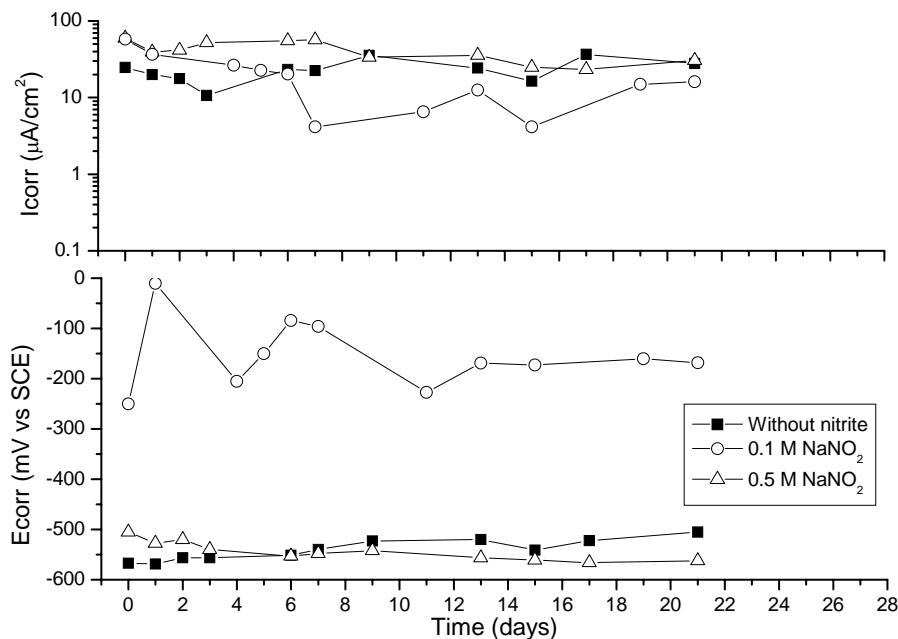


Figure 2. Evolution of I_{corr} and E_{corr} vs time in solutions of initial pH 7 with different concentration of sodium nitrite.

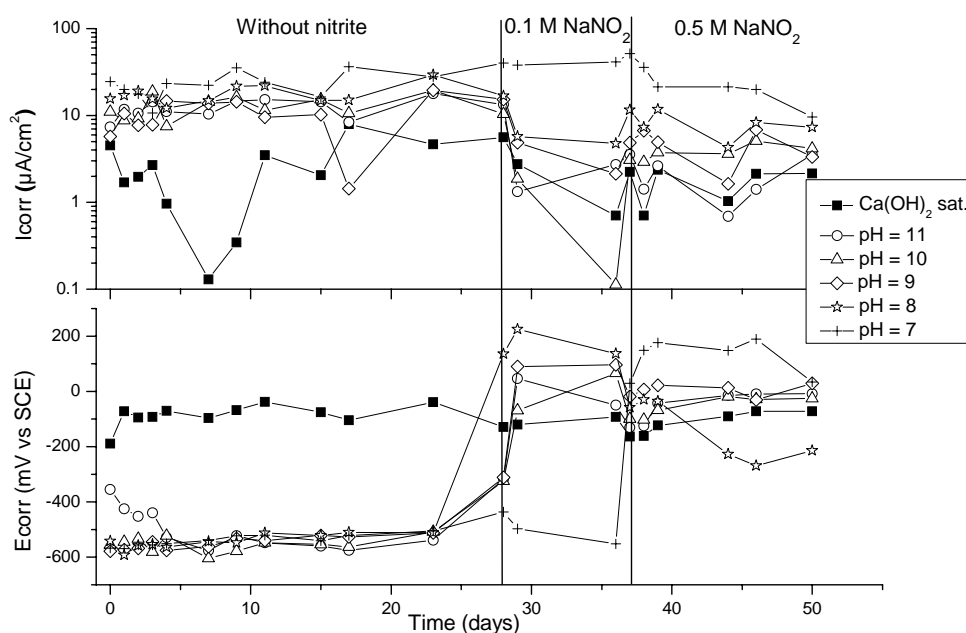


Figure 3. Evolution of I_{corr} and E_{corr} vs. time in solutions of initial pH with different additions of sodium nitrite.

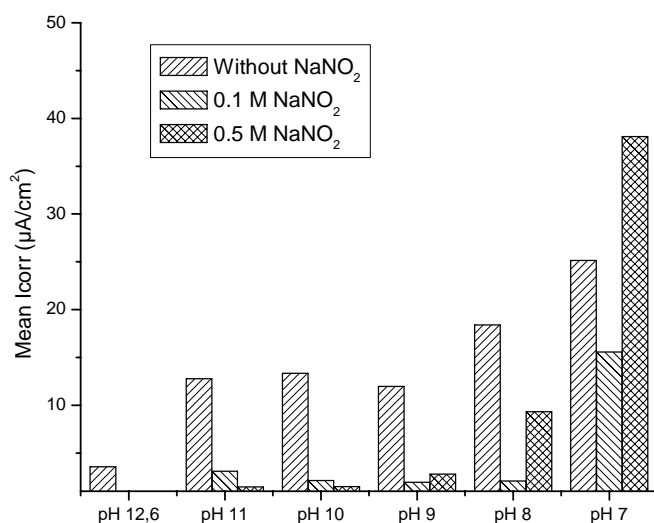


Figure 4. Evolution Mean I_{corr} values for different solutions and concentrations of NO_2^- .

Figure 4 presents Mean I_{corr} values for different pH and sodium nitrite concentration, respectively. It can be observed that a decrease in solution pH produces an increase in this parameter. Additionally it can be noticed that the addition of sodium nitrite in concentration of 0.1 M improves the corrosion rate of steels at any pH, and even reaches corrosion rate values of steels in saturated solution of calcium hydroxide between pH 11 and 8. If sodium nitrite concentration is increased up to 0.5 M, the decrease in Mean I_{corr} is similar or higher from pH 11 to pH 9. In pH 8 solution, although an improvement is observed respect to no addition of sodium nitrite, the inhibiting effect decreases. Finally, in pH 7 solution, the addition of such a high concentration of sodium nitrites does not show any inhibition of the corrosion process, even producing an increase in Mean I_{corr} respect to solution without inhibitor.

4 DISCUSSION

The dependence found of the Mean I_{corr} values on the initial pH of the solutions is shown in Figure 5. Figure 5 also depicts the values measured in previous works in a wide range of pH (Garcés et al. 2005, Garcés et al. 2008, Whitman et al. 1983).

In a previous work three main regions were distinguished. Data presented here lay in the basic and neutral region and they show a good enough fitting with previously reported data. In Figure 5 it can be observed that for a given pH, I_{corr} value can vary in one order of magnitude, although this scatter is similar in any pH region that is considered. Despite this scattering, the correlation between Mean I_{corr} and pH is clear.

In the acid region (pH < 5) the corrosion proceeds with gas (H_2) evolution and the I_{corr} increases as the pH lowers. This is attributed to several effects: a) higher H^+ concentration; b) the stirring effect of the gas evolution which facilitates the removal of the corrosion products from the metallic surface and c) the presence of oxygen which also enhances the corrosion current as two cathodic processes seem to occur (oxygen and H^+ reduction). A correlation can be found between I_{corr} values and pH when pH is below 5 (from literature data):

- For pH below 5: $\log I_{corr} = -0.3532 pH + 2.7632$

In the neutral region (pH between 5-9.5) the corrosion rate does not decrease greatly with the increase of the pH value. It remains more or less constant. It is reported that the overall process is the result of two opposite ones: a) the corrosion process producing ferrous ions able to hydrolyse the water molecules liberates protons and b) the precipitation of the $Fe(OH)_2$ formed which reduces the effective area suffering corrosion. The result is a certain buffering effect on the corrosion rate which remains rather constant in this pH range. A correlation can be found between I_{corr} values and pH when pH is between 5 and 9.5:

- For pH between 5 and 9.5: $\log I_{corr} = -0.1503 pH + 2.1793$

An additional correlation can be found in the basic region, for pH above 9.5. In this case, Figure 5 shows a sharp decrease of $\log I_{corr}$ when the pH is increased due to the passivation of the steel bars in such a basic environment. The tendency can be modeled by the following equation:

- For pH above 9.5 : $\log I_{corr} = -0.3520 pH + 4.4175$

When representing Mean I_{corr} values as a function of the $[Cl^-]/[OH^-]$ ratio, two instead of three regions can be identified as depicted in Figure 6. In the acidic and neutral regions, the Mean I_{corr} slightly decreases when lowering the $[Cl^-]/[OH^-]$ down to 10^2 . However, for values of $[Cl^-]/[OH^-] < 10^2$ (pH around 9.5) a steeper dependence of Mean I_{corr} with $[Cl^-]/[OH^-]$ is found showing a stronger competing character of both ions when the steel is covered with a passivating layer. It can then be deduced that, since reinforcing steel is present in the alkaline region, the I_{corr} values after depassivation increase one or two orders of magnitude when acidifying down to pH values around 9.5-10. For even lower pH values, the progressive increase of I_{corr} is less sensitive to the $[Cl^-]/[OH^-]$ ratio. So the following relations can be found according to these parameters:

- $[Cl^-]/[OH^-]$ ratio below 10^2 : $\log I_{corr} = 0.6721 \log \left[\frac{[Cl^-]}{[OH^-]} \right] - 0.4799$

- $[Cl^-]/[OH^-]$ ratio above 10^2 : $\log I_{corr} = 0.1820 \log \left[\frac{[Cl^-]}{[OH^-]} \right] + 0.0149$

The results obtained in this work fit in the trend observed in literature data indicating that, at the initial stage of the corrosion process, the addition of sodium nitrite can reduce the corrosion rate of reinforcing steels.

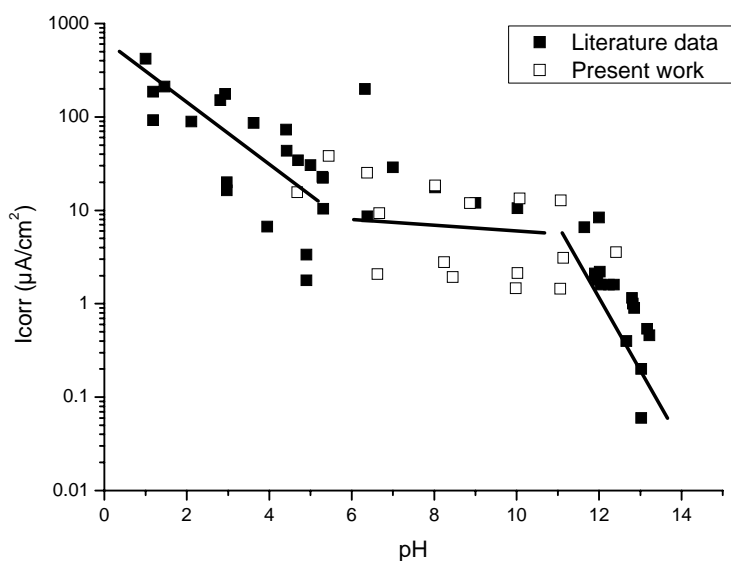


Figure 5. Influence of pH on the corrosion rate. Literature data from (Garcés et al. 2005, Whitman et al. 1983).

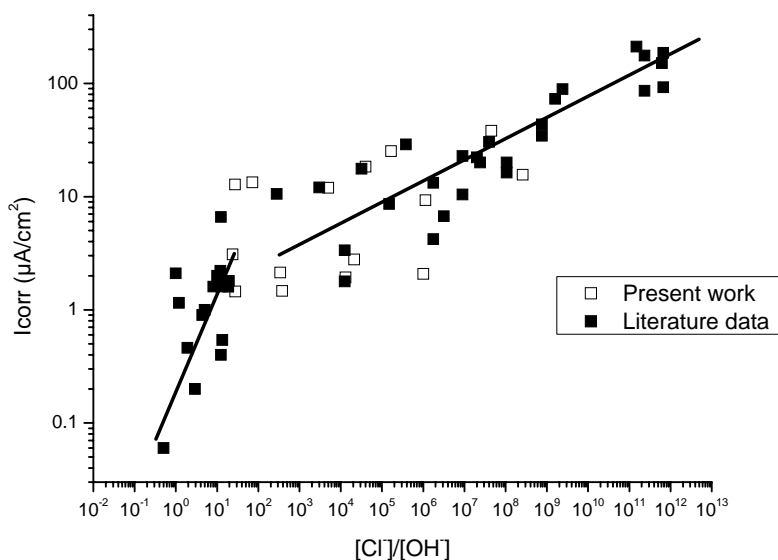


Figure 6. Relation between corrosion rate and $[Cl^-]/[OH^-]$ ratio. Literature data from (Garcés et al. 2005).

It has been observed that the presence of sodium nitrite in quantities up to 0.1 M produces an important decrease in the corrosion rate of steels in solutions from pH 11 to 7. These solutions could be related to the initiation period of the corrosion process, when chlorides are increasing their concentration at the steel surface and therefore, the passive layer is becoming weaker, although pits are not yet developed. Further addition of sodium nitrite up to 0.5 M provides a similar decrease in the corrosion rate of steels to that observed for sodium nitrite concentration of 0.1 M in solutions with pH ranging from 11 to 9. For solution of pH 8, the addition of sodium nitrite in concentration of 0.5 M reduces the corrosion level of the steels but in a lesser extent than the concentration of 0.1 M. Finally, for solution of pH 7, such a high addition of sodium nitrite makes corrosion rate worse even than no addition of sodium nitrite. Therefore, the addition of sodium nitrite in concentration of 0.1 M can reduce significantly corrosion rate at the initiation stage of the development of corrosion pits, so it can be deduced that initiation period would be longer due to the inhibiting effect of sodium nitrite. Higher concentration of sodium nitrite is not recommended since no signifi-

cant improvements or even worsening in corrosion rate are observed in addition to the higher expenses in chemicals.

5 CONCLUSIONS

The following conclusions can be drawn from this research:

- The addition of NaNO_2 has shown a significant inhibiting effect on the corrosion of steels in the initiation period when the chloride concentration is not very high, i.e., at the beginning of the initiation period to the beginning of the propagation period, although passivation is not attained by means of this addition.
- The efficiency of inhibition was very good when the quantity of NaNO_2 is not very high (0.1 M). Further addition of NaNO_2 does not improve significantly the results obtained by sodium nitrite concentration of 0.1 M and can even produce the contrary effect, increasing corrosion rates.

REFERENCES

- Alvarez M.G. & Galvele J.R. 1994. *Corrosion Science*, vol. 24, page 27.
- Andrade C. & Gonzalez J.A. 1978. "Quantitative measurements of corrosion rate of reinforcing steels embedded in concrete using polarization resistance measurements". *Werkst. Korros.*, vol. 29, page 515.
- Andrade C. & Page C.L. 1986. "Pore solution chemistry and corrosion in hydrated cement systems containing chloride salts. A study of cation specific effects". *British Corrosion Journal*, vol. 21, no. 1, pages 49-53.
- Andrade C. & Alonso C. 1996. "Corrosion rate monitoring in the laboratory and on-site". *Construction and Building Materials*, vol. 10, no. 5, pages 315-328.
- Anstice D.J. et al. 2005. "The pore solution phase of carbonated cement pastes". *Cement and Concrete Research*, vol. 35, no. 2, pages 377-383.
- Barnartt S. 1971. "Tafel slopes for iron corrosion in acidic solutions". *Corrosion*, vol. 27, no. 11, pages 467-470.
- Batis G. et al. 1996. "Durability of reinforced lightweight mortars with corrosion inhibitors". *Cement Concrete and Aggregates*, vol. 18, no. 2, pages 118-125.
- Garcés P. et al. 2005. "Corrosion of reinforcing steel in neutral and acid solutions simulating the electrolytic environments in the micropores of concrete in the propagation period". *Corrosion Science*, vol. 47, pages 289-306.
- Garcés P. et al. 2008. "Effect of nitrite in corrosion of reinforcing steel in neutral and acid solutions simulating the electrolytic environments of micropores in the propagation period". *Corrosion Science*, vol. 50, pages 498-509.
- Gorda V.K. 1970. *British Corrosion Journal*, vol. 5, page 198.
- Hoar, T.P. 1967. "Production and breakdown of passivity of metals" *Corrosion Science*, vol. 7, page 341.
- Janik-Czachor M. et al. 1975. *Corrosion Science*, vol. 15, page 775.
- Keddum M. et al. 1981. "Reaction model for iron dissolution studies by electrode impedance. 1. Experimental results and reaction model". *Journal of the Electrochemical Society*, vol. 128, pages 257-274.
- Lundquist J.T. et al. 1979. "Calcium nitrite as an inhibitor of rebar corrosion in chloride containing concrete". *Materials Performance*, vol. 18, no. 3, pages 36-40.
- Page C.L. & Treadaway K.W.J 1982. "Aspects of the electrochemistry of steel in concrete". *Nature*, vol. 297, no. 5862, pages 109-115.
- Page C.L. et al. 2000. "Corrosion inhibitors in concrete repair systems". *Magazine of Concrete Research*, vol. 52, no. 1, pages 25-37.
- Sideris K.K. & Savva A.E. 2005. "Durability of mixtures containing calcium nitrite based corrosion inhibitor". *Cement & Concrete Composites*, vol. 27, no. 2, pages 277-287.
- Stern M. & R.M. Roth. "Anodic behaviour of iron in acid solution". *Journal of the Electrochemical Society*, vol. 104, no. 6 (1957) 390-392.
- Whitman G.W. et al. 1983. *Industrial and Engineering Chemistry*, vol.16, no. 127, pages 665-670.