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Carbon steel passivity examined in alkaline solutions: The effect of chloride and nitrite ions

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Abstract

The effect of chloride and nitrite ions on the passivity of steel in alkaline solutions was investigated. Four nitrite dosages were tested, resulting in various nitrite/chloride ratios. The behavior of steel was evaluated on electrodes aged during 1 and 90 days, measuring electrochemical parameters such as the corrosion, pitting and repassivation potentials, the corrosion current density, the weight loss and performing electrochemical impedance spectra. The presence of 0.8 mol l^{-1} of chloride induced pitting only under polarization and when the chloride/hydroxyl ratio was not less than one. Nitrite ions behave as effective inhibitors of pit propagation for all the concentrations tested (0.2–0.8 mol l^{-1}). A nitrite/chloride ratio of 0.25 induces complete surface repassivation. Nevertheless, at open circuit potential, the high alkalinity guarantees passivation even in the presence of chlorides. In the event that the passive layer is damaged and pitting can be initiated, nitrite ions are effective in inhibiting pit propagation.

Keywords: Carbon steel; Alkaline solution; Corrosion inhibitor; Chloride; Nitrite

1. Introduction

In reinforced concrete, the bars acting as reinforcements (rebars) are usually low carbon steel bars. The steel is protected against corrosion because concrete provides a highly alkaline environment which guarantees that the metal remains in the passive state. But various contaminants have a detrimental effect on passivity. Among them, chloride ions are the most common ones and localized corrosion triggers when chlorides reach the metal surface. Chloride ions can be incorporated into concrete with seasand, or by using contaminated coarse aggregates, water or additives. Also, being concrete a porous material, chloride ions can penetrate from the atmosphere in structures placed in marine locations. This is certainly the case in many coastal cities in Argentina, where the use of seasand and contaminated aggregates and water constitutes a frequent practice. River sand or "clean" aggregates should be transported from far-away locations and markedly increase the construction costs.

Corrosion of rebars in concrete should be taken seriously from both, the economics and structural integrity standpoints. Many approaches can be used to mitigate the corrosion of reinforcing steel, among which protective coatings and sealers, cathodic protection, concrete realkalinization and corrosion inhibitors are commonly employed. The use of corrosion inhibitors is probably more attractive from the point of view of economics and ease of application [1]. Reviews of the most commonly used corrosion inhibitor types in concrete repair systems and the various possible mechanisms of inhibition have been recently published [2–4]. The most commonly used inhibitors are formulated on the basis of nitrite ions. It has been proposed that these ions react with ferrous ions generating a Fe_2O_3 protective layer, thus behaving as anodic inhibitors and decreasing corrosion rates [5,6]. However, when the surface is already passive, inadequate dosages of nitrite ions could enhance the risk of pitting [2,4,7].

When the passive state can be compromised due to the presence of chlorides, the corrosion risk is determined by the chloride content, usually evaluated as the chloride/hydroxyl ratio [8]. On the other hand, the efficiency of nitrite as inhibiting agent in the presence of chloride is evaluated in terms of the nitrite/chloride ratio. There is no clear agreement on the threshold value of

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this ratio. Different authors [2,4,9,10] have given values ranging from 0.34 to more than 1 as those necessary to prevent corrosion in concrete.

The corrosion of steel in concrete is difficult to investigate, mainly because of experimental problems such as high resistivities, highly porous materials, cell design and macrocells. An alternative way of tackling the problem is to use solutions that simulate the chemical environment present in the concrete pores. In this way, many investigations have been carried out in $Ca(OH)_2$ saturated solutions. However, the composition of concrete is much more complex [11,12]. Even when the results cannot be directly extrapolated to the situation in concrete, employing alkaline solutions is certainly a way of approaching the system, which has been extensively used [8,13–17], mainly because one is able to modify the relevant parameters one at a time.

The purpose of this investigation is to study the effect of nitrite ions on the breakdown of passive films formed on steel rebars in a highly alkaline electrolyte that simulates the solution present in chloride-contaminated concrete pores. It is our intention then, to evaluate if nitrite-base inhibitors can be helpful in controlling localized corrosion in good quality concrete prepared with contaminated aggregates. This condition will be used as reference for a work in progress where we are simulating the case of low quality concrete, where alkalinity is reduced due to the access of carbon dioxide through the concrete pores [18,19].

2. Experimental

2.1. Electrolyte composition

The experiments were carried out using an alkaline solution (AS). The composition of the AS was chosen to be KOH 0.6 $mol\,l^{-1}$, NaOH 0.2 $mol\,l^{-1}$ and $Ca(OH)_2$ 0.01 $mol\,l^{-1}$ with a resulting pH value of 13.9. This solution has been used before to simulate the electrolyte contained in concrete pores [20].

To evaluate the inhibitor effect, various concentrations of $NaNO_2$ (0.2, 0.4, 0.6 and 0.8 $mol\,l^{-1}$) were added to the alkaline solution where indicated.

To simulate a concrete contaminated with chloride ions, AS solutions incorporate 0.8 $mol\,l^{-1}$ NaCl where indicated.

2.2. Electrodes preparation

Samples were prepared from steel reinforcement bars (Mn 0.635%, C 0.299%, Si 0.258%, Cu 0.227% and others impurities 0.245%). They were cut into disks with an area of 0.214 cm^2, provided with an electrical contact and embedded in Teflon bodies. The resulting electrodes were polished down to grade 1000 with emery paper. They were rinsed with distilled water prior to performing electrochemical measurements.

On the other hand, coupons with an area of 7.22 cm^2 were prepared and also polished down to grade 120 with emery paper. When used for electrochemical determinations, the coupons were held conveniently and the electrochemical cell was used with a fixed volume to guarantee a constant exposed area of 5.45 cm^2.

2.3. Weight loss determinations

Weight Loss Method was applied following the guidelines in ASTM D 2688 Standard Test Methods for Corrosivity of Water in the Absence of Heat Transfer. Previously weighted coupons were suspended and immersed in each testing solution, placing five coupons in each of ten containers. The metal samples were polished down to grade 120 with emery paper. The containers were kept at room temperature, with gentle agitation to avoid differential deaeration. Some coupons were withdrawn for each container after 90 days and the corrosion products were stripped by immersion in HCl 10%. Then they were neutralized with saturated Na_2CO_3 solution, and finally rinsed with distilled water. The clean and dry coupons were weighted and observed with a metallographic microscope.

The remaining coupons were employed for electrochemical tests.

2.4. Electrochemical techniques

A three-electrode electrochemical cell was used. A Hg/HgO electrode with 1 $mol\,l^{-1}$ KOH solution (labelled as MOE, $E = 0.123$ V vs. NHE) was used as reference. All the potentials are indicated against this electrode. A platinum wire of large area was used as counter electrode.

All the experiments were carried out with a Voltalab PGP 201 potentiostat.

Cyclic voltammograms were recorded after deaerating the electrolyte by bubbling N_2 during 15 min prior to each measurement. The electrodes were pre-reduced at −1.1 V for 5 min. Finally the scan was started at −1.1 V and reversed at 0.50 V or at convenient potential values, as indicated. The sweep rate used was $1 \times 10^{-2}\ V\,s^{-1}$.

The open circuit potential (OCP) was measured during 24 h in the different conditions investigated.

Polarization resistance (Rp) was evaluated as $\Delta V/\Delta j$, from potential sweeps scanning ±0.01 V from the OCP at a scan rate of $1 \times 10^{-4}\ V\,s^{-1}$. Average values of over five individual experiments were obtained in the case of samples aged for 1 day, while duplicates were evaluated for coupons immersed during 90 days.

Corrosion rate, in terms of corrosion current density, can be evaluated from the polarization resistance data according to the Stern–Geary relationship as [21]:

$$j_{corr} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \frac{1}{Rp} = \frac{B}{Rp} \qquad (1)$$

where β_a and β_c are the anodic and cathodic Tafel slopes, respectively. These are kinetic parameters characteristic of each metal–solution system.

Assuming uniform corrosion on the entire metallic surface, the nominal value of corrosion rate (CR) in $\mu m\,year^{-1}$ can be calculated using Faraday's law as:

$$CR = \frac{K a_W}{n F \delta} j_{corr} = \alpha j_{corr} \qquad (2)$$