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Electrochemical Impedance Spectroscopy Study on Corrosion Inhibitor for Reinforced Concrete

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In this essay, electrochemical impedance spectroscopy (EIS) was applied to investigate the behavior of steel at diverse phases during corrosion. The evolution of obtained spectra manifested the start of partial corrosion of steel and the gradual inhibition with different concentrations of the inhibitor. Calcium nitrite was found to have the capacity to inhibit the steel corrosion, and the best inhibitor efficiency was investigated for $[Cl^-]/[NO_2^-]$. If the value of this rate was attained in the initial phases of the corrosion course, the inhibition efficiency would be higher. Calcium nitrite has excellent effectiveness when used as a penetrating corrosion inhibitor for steel in concrete.

Keywords: Calcium nitrite; Electrochemical impedance spectroscopy; Corrosion inhibitor; Reinforced concrete; Penetration

1. INTRODUCTION

The concept of “corrosion of reinforced concrete” refers to both the issues of reinforcement corrosion and the state of more or less rebar defense by concrete itself. There are two methods for the protection of steel in concrete: a physical obstruction made by a blanket layer or the production of a passivation film on the rebar originating from the chemical reaction occurring in the concrete with typical pH [1, 2]. In addition to double protection, other factors contribute to the evolution of corrosion in concrete, such as the decline of covering layer thickness, less resistance to CO_2 penetration, the existence of water and salts in the covering layer of concrete, weak seal or vibration of the concrete, pollution from salts or gases such as SO_2 or CO_2, the existence of sulfate-reducing bacteria, the decline of cement substance and the improvement of the water/cement ratio. In fact, the corrosion course of reinforced concrete is obscure since the initial indications of corrosion appear long after the start of this process. As a result, it is very difficult to identify it in the initial stage [3-9].

In practice, a good way to control steel corrosion in concrete is the application of corrosion inhibitors [10, 11]. Preventive and curative treatments have high potential to be very effective, depending on the mode of inhibitor application. Preventive treatment exists in the process of introducing corrosion inhibitors within mixing water to the newly placed concrete. The inhibitors are used to reinforce the passive film on the embedded steel. It is advisable to postpone the initiation of steel corrosion in cases where the pollution of chloride and/or carbonation begins and ultimately reduces the rate of the corrosion [12-14]. The application of this protection method can be dated to a few decades ago, and it is well established. Curative treatment exists in the use of corrosion inhibitors directly on the cover of the corroding concrete structures, which are exploited and consolidated [15-18]. This kind of inhibitor is known as a penetrating or migrating inhibitor. It is believed that these inhibitors can penetrate the blanket of the concrete to the strengthened steel and then inhibit the ongoing steel corrosion. In the last two decades, the application of permeating corrosion inhibitors to steel in concrete has become very popular. This protection mechanism is thought to be a convenient and economical method to revive the protective nature of carbonated concrete or concrete polluted by chloride. Nevertheless, the published data with respect to the performance of these inhibitors arouse both expectations and great doubts [19]. In the cement mix water, nitrite is added as its calcium salt. There is some research about the performance of nitrite ions in postponing the initiation of corrosion [20, 21]. Since the passivating oxide layer of compounds formed by steel with ferrous ion can be undermined by chloride, a complicated cycle of oxygenation and transport appears, resulting in the development of extended corrosion products. The suppression of this cycle can be accomplished by means of adding a suitable dose of nitrite ions that can react with compound ferrous ions, known as a vital intermediate element. As an anodic inhibitor, calcium nitrite can oxidize ferrous ions, namely, the first product of the corrosion process, into ferric ions quickly, and then, it will undergo precipitation under the environment of alkaline pH in concrete, leading to interruption of the corrosion cycle [22]**.**

A variety of techniques can be used to assess and investigate corrosion in strengthened concrete, among which the most widely used is electrochemical techniques. These techniques not only have the function of analyzing corrosion by regarding it as an electrochemical phenomenon but also have an advantage over other techniques, namely, their fast speed and damage-free nature in the application process. In addition, their application can be realized in both the field and the lab. Electrochemical impedance spectroscopy (EIS), an effective method for describing the features of various electrochemical mechanisms, can be used to determine what contributions electrode processes have made in these mechanisms [23]. EIS can be adopted to study the dynamics of connected or mobile charges on the volume of the interface domain or any liquid or solid substance. It is assumed that the elaborate circuit can manifest the action of the steel tumbled in the concrete. In this paper, research on the capacity of calcium nitrite to suppress the steel corrosion triggered by chloride was undertaken. The implementation of measurements was conducted in solutions imitating diverse phases of the curative treatment by using permeating corrosion inhibitors. Moreover, the influence of the phase on the corrosion process was also evaluated. EIS was applied to investigate the behavior of steel at diverse phases in the process of corrosion and suppression.

2. EXPERIMENTS

2.1. Materials

Two series of tests were conducted with different addition methods of calcium nitrite. The time dependence of $[Cl^-]/[NO_2^-]$ in the two series of tests was described. There was a relatively high concentration of inhibitor in series CA I. As a result, the ultimate value of this rate, 0.33, was achieved 4 weeks after the onset of the steel corrosion. In contrast, there was a relatively low concentration of the inhibitor in series CA II. The achievement of the same value of $[Cl^-]/[NO_2^-]$ ratio was reached 11 weeks after the onset of the steel corrosion process. The steel electrodes comprised structural carbon steel bars whose diameter was 8 mm, and approximately 19 cm^2 of the superficial area was exposed to the solution. The steel surface was treated in the following way. First, it was polished by using emery paper within the range of 120-220 grit. Second, it was skimmed by acetone. Finally, it was rinsed through methanol.

2.2. Strength and setting time measurement

The compressive strength of the concrete with corrosion inhibitors was evaluated on cylinder-shaped samples whose length and diameter were 200 mm and 100 mm, respectively. The mix ratio of the development of samples was 370 kg/m^3 OPC, 1055 kg/m^3 10 mm coarse aggregate (density: 2.71), and 787 kg/m^3 fine aggregate (density: 2.61). If the water content in the corrosion inhibitors was considered, the ratio of free water/cement was 0.5. In the test on coagulation time and ion penetrability, this concrete mixture could be applied as well. The addition of corrosion inhibitors was 0, 3, 6 or 12%. When the demolding was accomplished, the samples were cured in a 95% humidity cabinet at the temperature of 20 °C. The penetration resistance determined the setting time. With the use of a sieve, a mortar was acquired after the coarse aggregate was removed from green concrete. The initial condensation refers to the time when the penetration resistance reached 35 kg/cm^2, while the last set refers to the achievement of 280 kg/cm^2.

2.3. Permeability measurement

To evaluate the penetrability of concrete with the addition of corrosion inhibitors, rapid chloride permeability tests were employed. A concrete disc whose thickness and diameter were 50 mm and 100 mm, respectively, was connected with dual chambers: one was full of 3% sodium chloride solution, while the other one was filled with 0.1 M sodium hydroxide for the purpose of developing electrodes. The electric charge of the electrodes was 60 V for 6 h. The current circulating inside the concrete samples and the solution temperature in the chamber were supervised every half hour. Later, to ascertain the permeability, the overall charge circulating through the cell was determined. This indicated that the level of charge circulated was positively related to the concrete penetrability.

2.4. EIS measurement

With the help of electrochemical impedance spectroscopy utilizing the Autolab mechanism, which has specialized software, the observation of the corrosion action of steel in the process of these tests was achieved. The measurements were finished at the corrosion potential, and the amplitude of the sinusoidal wave interference was 10 mV within the frequency scope of 50 kHz to 0.5 Hz and 30 mV within the frequency scope of 0.5 Hz to 0.5 MHz. The obtainment of ten points in each frequency decade was achieved. If a high amplitude was applied when the frequencies were low, it would lead to the decline of noise appearing in the high-impedance mechanism within this frequency scope. The saturated calomel electrode was employed in a critical reference role, while the opposite electrode was a large corrosion-resistant plate (approximately 100 cm^2). EIS measurements were carried out when the prepassivation stage was over, namely, after the start of steel corrosion in solutions containing chloride, one week after every increase in the concentration of inhibitors, and upon every decline of the chloride/nitrite ratio. Impedance data obtained from the solution free of inhibitors were used as references for determining the inhibition efficiency. For each test, there were 3 samples, and the average of the obtained values was considered as well. The variability of the data was signified through the standard deviation estimate.

3. RESULTS AND DISCUSSION

Specimens were prepassivated in the solution saturated with $Ca(OH)_2$ before the addition of calcium nitrite. Later, these specimens were placed in the same solution with 1% NaCl. When these treatments were finished, the contrast of impedance spectra (in the form of Bode) was performed, as shown in Figure 1. The development of a passive film on the steel surface was proved by the capacitive response, namely, a wide and unsymmetrical peak of the phase angle and high values of the steel’s low frequency impedance. Remarkable variation in impedance data was found later when prepassivated steel was placed in the chloride-based solution. The higher conductivity of the solution contributed to the decline in impedance values at high frequencies. Other variations existing in the impedance spectrum, such as the capacitive response at low frequency, the shift of a wide peak of the phase angle to higher frequencies, and the dramatic decline in impedance values at low frequencies, confirmed that the corrosion was initiated. Higher maximum phase angles were also observed in the presence of the inhibitors, reflecting a capacitive behavior related to the increase of polarization resistance in the presence of the inhibitor [24]. From the phase angle, which is unsymmetrical to a great extent, it can be seen that there is an overlapping of double time constants. This kind of impedance action is caused by the initiation of partial steel corrosion [25].

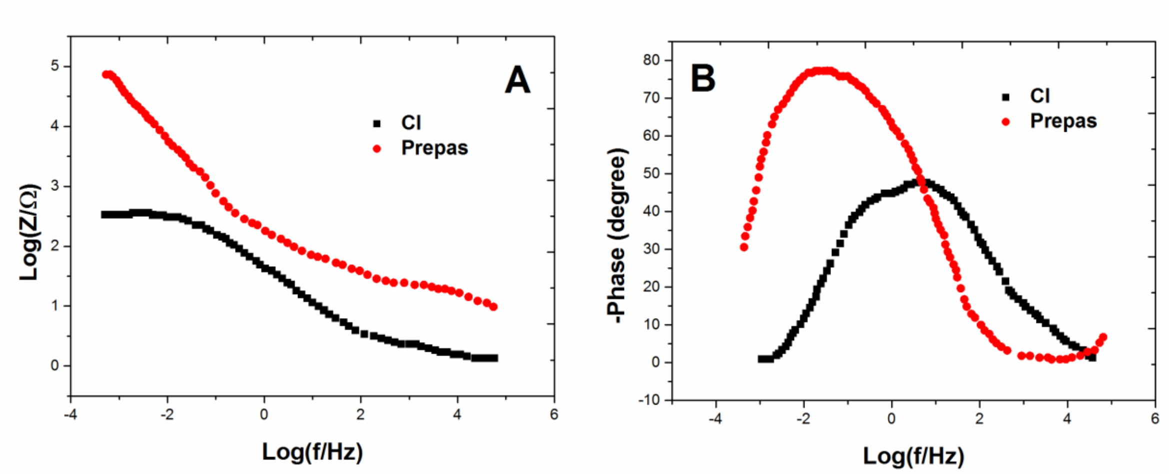

Figure 1. Bode diagrams for steel when the prepassivation and the corrosion onset finished (Cl): (A) impedance module and (B) phase displacement.

Figure 2 describes the outcomes of the rapid ion penetration test, revealing the lumped-charge flowing through concrete samples for 6 h. Compared to the control sample, the corrosion inhibitor was found to have the function of improving the total charge. The values of the charge passed for the 3% corrosion inhibitor varied from 7855 to 9891 C, while the control specimen produced 6437 C. Through the observation, the conclusion was reached that the temperature in the chambers of every cell increased in proportion with the lumped charge. The main cause of this is that a direct current (DC) of 60 V produced heat that accelerates the circulation of ions in turn. The temperature has a great influence on the mobility of ions.

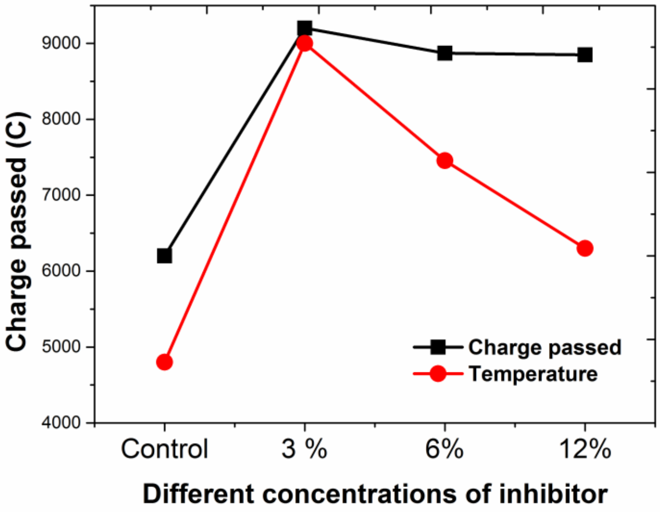

Figure 2. Temperature of chambers and lumped-charge flowed through concrete samples with the addition of corrosion inhibitors in a rapid method of ion permeation.

The strength of concrete with the addition of corrosion inhibitors was approximately 10% greater than that of samples without any inhibitor. In the early phases, calcium nitrite was found to have a positive effect on the improvement of concrete strength. As a result, it can be seen that calcium nitrite, to say the least, is free from negative effects in the early formation of compressive strength. Nevertheless, this condition changed after 100 days, and the strength was determined by whether there was an addition of the corrosion inhibitor. After 100 days, the control concrete's compressive strength was improved slightly in comparison with that at 60 days, while that of concretes with the addition of corrosion inhibitor declined within the scope of 386-401 kg/cm^2, which was the same as the values at 28 days. This might be the result of calcium chloro-aluminate formation due to chloride that was chemically bonded by reactions with the C_3A compound of the Portland cement [2, 26].

The finding that the application of the calcium nitrite-based corrosion inhibitor is likely to have a negative impact on the development of strength in the long run may bring challenges to previous research. Through this study, the coagulation time with calcium nitrite was identified. Addition amounts of corrosion inhibitors were 0, 3, 6 and 12%. Figure 3 shows that the setting time was adversely related to the addition amount of the corrosion inhibitor. In the control concrete, the primary and final set times were 5 and 7 h, respectively, while for the concrete with the corrosion inhibitor whose concentration was 12%, they were 4.2 h and 6.1 h, respectively. If the setting time declined, it signified not only the improvement of heat production during cement matrix hydration but also the reduction of the time for site work.

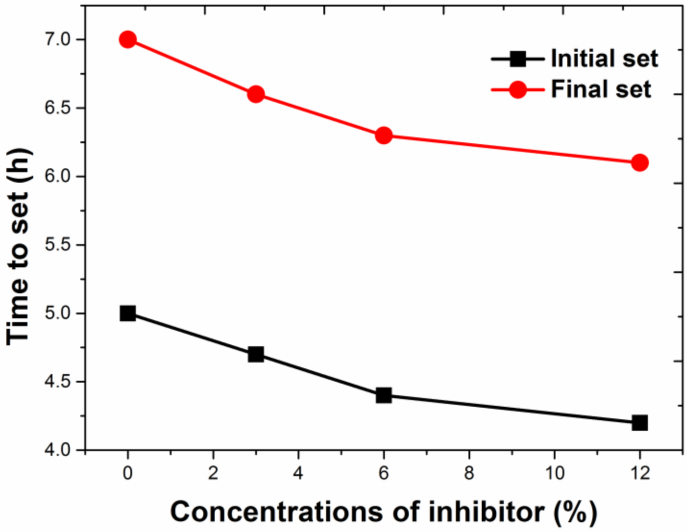

Figure 3. Coagulation time for 0, 3, 6 and 12% calcium nitrite.

The most important point of such long-term tests is pH control. In the process of the carbonation of alkaline solutions, the pH decreases, and this change can play a role in steel's corrosion behavior. The changes of pH in solutions whose inhibitor concentration was increasing gradually can be seen in Figure 4. The initial pH values were between 11 and 12. Conceivably, the decline of pH was caused by the carbonation of alkaline solutions that underwent 3 days of prepassivation and primary exposure after chloride addition. As shown in Figure 4, a further gradual decline of pH value resulted from the further carbonation and the growing concentration of calcium nitrite, while the sharp rises were in accordance with the modification behavior of the applied pH, namely, the addition of

$Ca(OH)_2$. It is generally accepted that the passivity breakdown potential and induction time on metal and alloy surfaces in aqueous solutions are distributed parameters [27]. It should be emphasized that though we modified the pH, we still failed to prevent overmuch variations in pH, for series CA I in particular. The high frequency of pH measurements that led to the stirring of test solutions seemed to speed up the carbonation. Ultimately, the pH in the first series declined to approximately 11, compared to 12 at the onset of this test. In contrast, in the second series, despite primary fluctuations, the pH value maintained its stability at approximately 12.

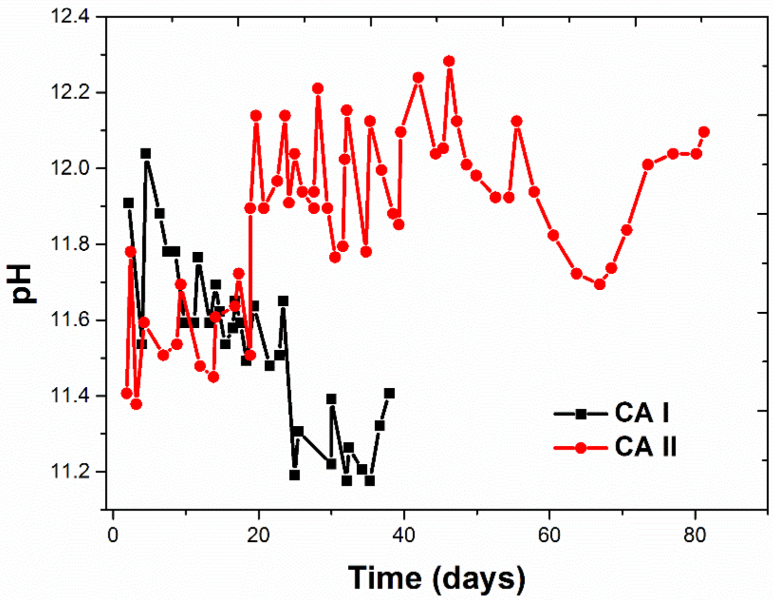

Figure 4. The time dependence of pH value for solutions in the CA I and CA II tests.

Figure 5 describes the development of the impedance spectra of series CA I. To evaluate the impact of inhibition, the spectrum for steel with initiated corrosion was obtained as a reference. The addition of calcium nitrite ($[Cl^-]/[NO_2^-] = 1.5$) for the first time led to remarkable improvement in the impedance at low frequency and a more capacitive response with two obvious time constants. Through this, some inhibition of steel corrosion was confirmed. These variations were remarkable after the addition of inhibitor ($[Cl^-]/[NO_2^-] = 0.77$) for the second time. The capacitive degree of the response was much higher. In the phase angle, a sharp decline was observed, which revealed high values in a broad frequency domain. In addition, the impedance modulus's frequency dependence was in a linear form until the lowest frequencies; at the same time, the impedance values at low frequency were higher to a great extent. This behavior was likely related to steel repassivation. These variations were in conformity with the chloride-to-nitrite ratio under 1. Fourteen days after the primary addition of the inhibitor, this threshold rate was attained in series CA I. The following addition of calcium nitrite and ongoing decline of the $[Cl^-]/[NO_2^-]$ ratio were effective to some extent. The impedance spectra had almost no change. As a result, further improvement through the addition of inhibitors was unpractical under this circumstance.

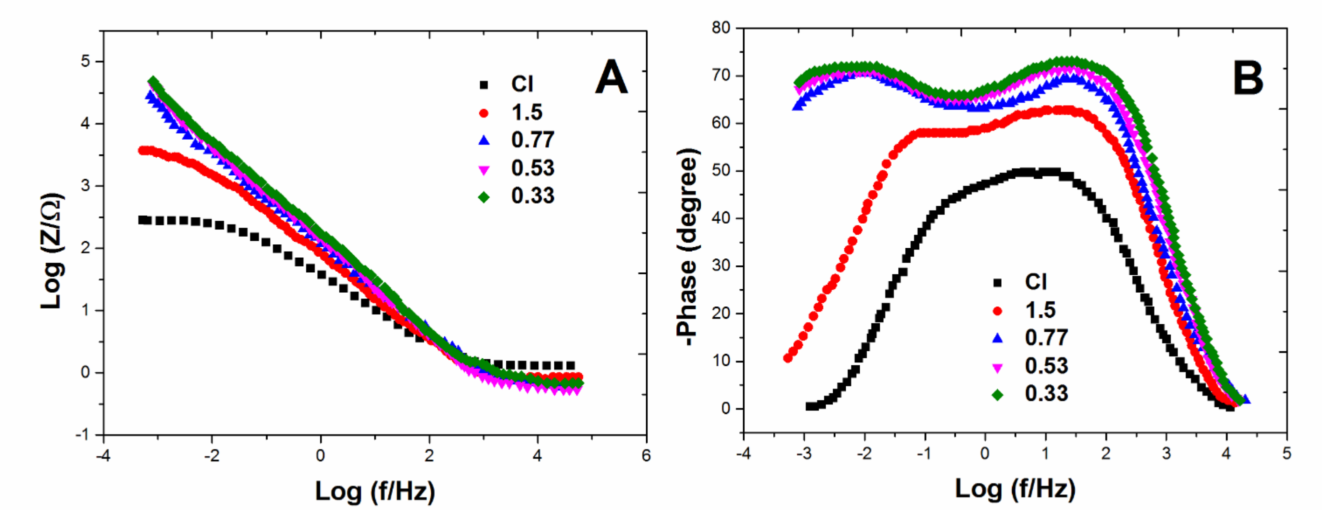

Figure 5. Evolution of impedance spectra for steel during test CA I: (A) modulus of impedance and (B) phase shift. Values of the $[Cl^-]/[NO_2^-]$ proportion are specified in the spectra.

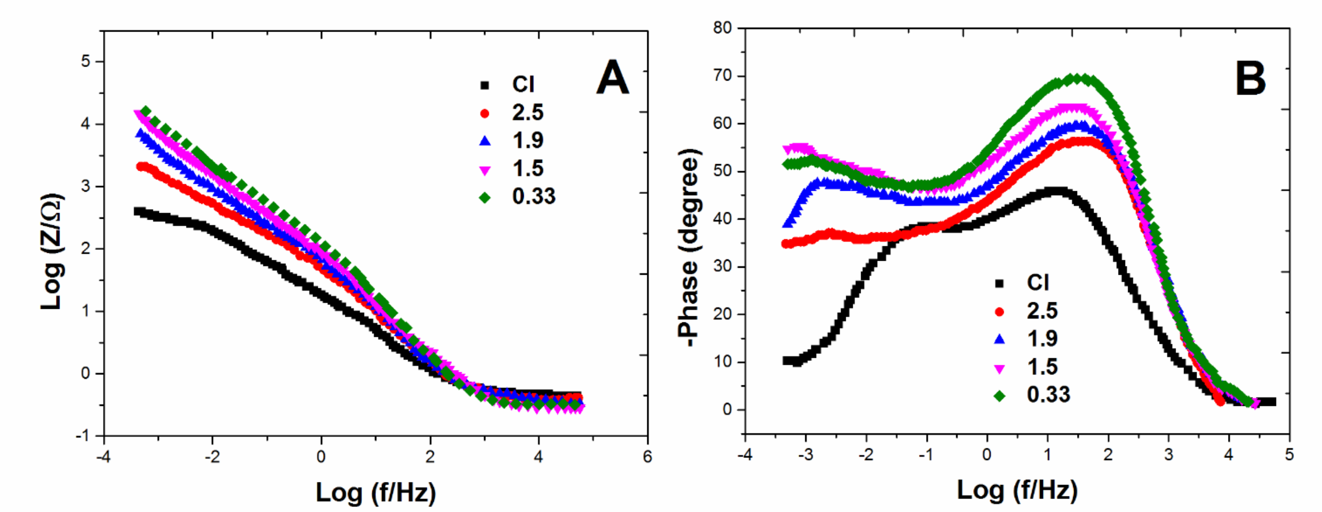

Figure 6. Development path of impedance spectra for steel during test CA II: (A) modulus of impedance and (B) phase shift. Values of the $[Cl^-]/[NO_2^-]$ proportion are specified in the spectra.

Figure 6 depicts the impedance data obtained from the test series CA II. Here, the concentration of the inhibitor was low. Minor changes of impedance data, which correspond to a slight rise in the impedance modulus and the phase angle at low frequencies, were found even when the concentration of calcium nitrite ($[Cl^-]/[NO_2^-] = 7.5$) was very low. Nevertheless, rusty trails outflowing from corrosion areas were observed at this phase of the test. Subsequent additions of calcium nitrite (until $[Cl^-]/[NO_2^-] = 1.5$) led to a slight rise in low-frequency impedance and an elevation of the phase angle. In addition, at low frequencies, a diffusion tail was revealed. This finding showed that the inhibition degree was low and that the diffusion control of the corrosion course was initiated. At that time, the rusty trails were not observed. Interestingly, increasing concentration of inhibitor (only the spectrum for the final addition corresponding to $[Cl^-]/[NO_2^-] = 0.33$ is revealed) failed to alter this state radically. Unlike in series CA I, whose low-frequency impedance values were much higher, an obvious decline in the phase angle could not be found in series CA II. Therefore, the efficiency of inhibition was lower here. Considering the ascending trend of impedance values and, accordingly, the polarization resistance with increasing concentration of both inhibitors, exhibited in the Bode-modulus part, it is confirmed that calcium nitrite could increase the corrosion resistance of the samples [28, 29]. Nevertheless, it should be noted that the time span of series CA II from the start of corrosion to this moment when the ratio of chloride to inhibitor is less than 1 is 5 weeks longer than that in series CA I, namely, 2 weeks.

The fitting results are described based on the $[Cl^-]/[NO_2^-]$ ratio, whose values are manifested on the axis in inverted order. This signifies that the addition of inhibitors increases from left to right. A gradual decline in the solution resistance R_s and the ratio of $[Cl^-]/[NO_2^-]$ (as shown in Figure 7) is equal to the increasing addition of calcium nitrite when the concentration of NaCl remains unchanged. In the two series, the results obtained are very similar.

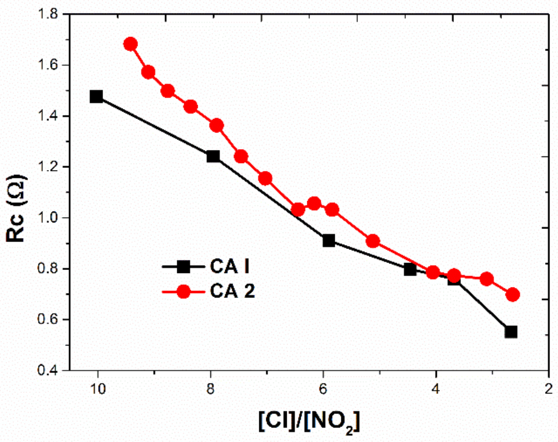

Figure 7. The association between the solution resistance R_s and the proportion of $[Cl^-]/[NO_2^-]$ for the two tests.

4. CONCLUSIONS

In sum, calcium can suppress the initiated partial corrosion of consolidated steel in solutions simulating concrete polluted by chloride if its concentration is sufficient in the initial phases of the corrosion process. Repassivation of steel occurred when the ratio of chloride to nitrite was less than 1. In addition, both this ratio and the phase of corrosion development are the determining factors of the inhibition ability of calcium nitrite in the steel corrosion process.

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