Role of Carbon Dioxide on the Corrosion of Carbon Steel Reinforcing Bar in Simulating Concrete Electrolyte

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Abstract:
The main factors that make it possible to get the corrosion of reinforcing steel in concrete are chloride ions and the absorption of carbon dioxide from the environment, and each of them works with a mechanism which destroys the stable immunity of rebar in the concrete. In this work the effect of carbon dioxide content in the artificial concrete solution on the corrosion behavior of carbon steel reinforcing bar (CSRB) was studied, potentiostatically using CO\textsubscript{2} stream gas at 6 level of concentrations; 0.03 to 2.0 weight percent, and the effect of rising electrolyte temperature was also followed in the range 20 to 50\textdegree C. Tafel plots and cyclic polarization procedures were obeyed to investigate the corrosion parameters and pitting susceptibility respectively. The change in the microstructure and morphology of the CSRB after polarization in the simulate concrete solution was studied using optical and atomic force microscopes. The results show that the corrosion rate of the CSRB in artificial concrete greatly increases with the existence of CO\textsubscript{2} gas and highly depends on its concentration in the range 0.03 to 2.0\%. No sign for pitting corrosion is recorded at all CO\textsubscript{2} concentrations and the general corrosion is the main problem in the conditions under consideration.

Key words: Artificial concrete, CO\textsubscript{2} gas, Concrete solution, Steel reinforcing.

Introduction:
Concrete structures such as bridges, reservoirs, and residential buildings are designed to last for decades, and their collapse is mainly due to the corrosion of the used reinforcing carbon steel (1-3), although the basic environment of the concrete structure provides self-protection by producing a very thin passive film which limits the metal loss from the carbon steel surface (4,5). Several studies have shown that the main cause of the destruction of the protective passive layer of carbon steel in concrete is chloride ions, carbon dioxide and other atmospheric pollutants and will corrode faster (6-10).

This work focuses on examining the effect of increasing the concentration of carbon dioxide on the rate of corrosion of steel rebar. It depends on temperature, and the probability of pitting corrosion.

Table 1. Chemical composition of carbon steel reinforcing bar (CSRB) used in this study

| Element | C | Si | N | Cu | Mn | Ni | Cr | p% |
|---------|---|----|---|----|----|----|----|----|
| %       | 0.2| 0.0| 0.2| 0.0| 0.2| 0.73| 0.1| 0.1|
|         | 6  | 31 | 8  | 10 | 8  | 3   | 2  | 8  |

For corrosion measurement, the CSRB was pickled first with concentrated HCl (37%, luka /Switzerland), then rinsed with running water then ethanol and dried well, an adhesive tape was used to cover all steel rebar except for a known surface area that is (16.55cm\textsuperscript{2}), Fig. (1).

Figure 1. Preparation of the Carbon steel reinforcing bar used in this study.
The steel rebar was immersed in three electrode cells and served as working electrode, the Pt-electrode served as counter electrode, and Ag/AgCl as references electrode, the CO₂ gas was introduced to the corrosion cell through porcelain bubblier from CO₂ gas cylinder (BOC, UK), Fig.(2).

![Figure 2. The electrochemical cell for corrosion measurement of carbon steel reinforcing bar in simulates concrete solution](image1)

The gas concentration was calculated by multiplying the value of the flow rate (cc/min) of CO₂ gas stream and time (min) of passing the gas, then estimating weight of the CO₂ gas from the number of moles of the gas. The open circuit potential (OCP) was measured using Potentiostat (Mlab200, Bank Elektronik Intelligent control, Germany) and then the CSRB was polarized in the simulate concrete solution (Ca(OH)₂ (2gm), KOH (22.44mg), NaOH (8mg) in 1L of distill water) after passing the required concentration of CO₂ gas (0.03, 0.26, 0.50, 1.00, 1.50, and 2.00%). After that, Tafel plots were recorded for corrosion rate measurement by scanning the potentials ±200mv around the OCP with a rate of 2mv/sec, the same procedure was repeated at four temperatures; 20, 30, 40, and 50°C.

The cyclic polarization was conducted at 20°C starting from few millivolt lower than OCP going up to about 1000mv. The change in the microstructure and morphology of the surface was followed by optical microscope (Nikon Eclipse ME 600, Japan) and atomic force microscope (SPM AA3000, Angstrom Advanced Inc., USA) respectively.

**Results and Discussion:**

Figure 3 shows Tafel plots of carbon steel reinforcing bar (CSRB) in artificial concrete solution with and without different CO₂ gas concentrations at different temperature.

![Figure 3. Tafel plots of carbon steel reinforcing bar in artificial concrete solution containing different CO₂ concentration at 20, 30, 40, and 50 C.](image2)
From these Tafel plots the corrosion current density (i_corr), corrosion potential (E_corr), anodic Tafel slopes (β_a) and cathodic Tafel slopes (β_c) were estimated and then used to calculate the polarization resistance (R_p) using Eq. (1) the corrosion rate as which is often converted into Faradaic corrosion rate having units of (mm/y).

\[ R_p = \frac{1}{2303 (i_{corr})(β_a + β_c)} \]  

All corrosion parameters are tabulated in Table 2, the corrosion rates of the CSRB in concrete solution with and without CO_2 at all temperatures were calculated by Faraday's laws equation 2. 

\[ m = \frac{(Q/F)}{(M/n)} \]  

Where:  
\( m \): is the mass of the substance liberated or deposited at an electrode in grams,  
\( Q \): is the total electric charge passed through the substance,  
\( F \): 96500 C mol\(^{-1}\) is the Faraday constant,  
\( M \): is the molar mass of the substance,  
\( n \): is the valency number of ions of the substance (electrons transferred per ion). Reflected small values (0.28-0.71 mm/y) which attributed to the inert immunity of the concrete solution due to high pH value (12).

| CO2%  | T(K) | E_corr (mV) | i_losr \((10^4)\text{cm}^2\) | βc (mV/Dec) | β_a (mV/Dec) | R_p \((Ω/\text{cm}²)\) | CR(WL) \text{g/m}²\text{d} | CR(PL) mmpy |
|-----|-----|------------|-----------------|-------------|-------------|----------------|----------------|-----------|
| 0.00 | 293 | -340.3 | -121.8 | 137.1 | 1175.29 | 6.05 | 0.281 |
| 303 | -379.6 | 31.47 | -129.4 | 176.8 | 1030.91 | 7.87 | 0.365 |
| 313 | -421.1 | 39.04 | -89.8 | 166.6 | 648.97 | 9.76 | 0.453 |
| 323 | -393.2 | 61.45 | -82.7 | 186.4 | 404.78 | 15.40 | 0.713 |
| 0.03 | 293 | -698.4 | -69.7 | 48.9 | 85.92 | 36.30 | 1.69 |
| 303 | -718.7 | 182.76 | -69.8 | 44.3 | 64.38 | 45.70 | 2.12 |
| 313 | -712.0 | 196.91 | -62.5 | 44.0 | 56.94 | 49.2 | 2.29 |
| 323 | -713.8 | 231.43 | -67.5 | 51.3 | 54.68 | 57.9 | 2.69 |
| 0.26 | 293 | -644.4 | 177.21 | -63.2 | 60.5 | 75.73 | 44.3 | 2.06 |
| 303 | -676.5 | 192.55 | -81.3 | 66.3 | 82.35 | 48.1 | 2.23 |
| 313 | -619.6 | 208.04 | -239.6 | 201.7 | 228.56 | 52 | 2.41 |
| 323 | -690.8 | 258.67 | -77.1 | 62.9 | 58.14 | 64.7 | 3.00 |
| 0.5 | 293 | -475.4 | 185.26 | -117.8 | 131.6 | 145.68 | 46.3 | 2.15 |
| 303 | -432.5 | 195.82 | -83.2 | 74.3 | 87.03 | 49 | 2.27 |
| 313 | -472.4 | 210.59 | -86.2 | 87.9 | 89.73 | 52.6 | 2.44 |
| 323 | -394.4 | 75.79 | -117.4 | 300.1 | 483.47 | 18.9 | 0.88 |
| 1.0 | 293 | -534.0 | 192.36 | -99.9 | 124.6 | 125.15 | 48.1 | 2.23 |
| 303 | -370.6 | 210.24 | -63.5 | 64.4 | 66.03 | 52.6 | 2.44 |
| 313 | -387.6 | 215.82 | -48.8 | 67.0 | 56.80 | 54 | 2.50 |
| 323 | -403.5 | 276.25 | -41.4 | 90.6 | 44.66 | 69.1 | 3.21 |
| 1.5 | 293 | -438.4 | 212.49 | -74.8 | 79.9 | 78.94 | 53.1 | 2.47 |
| 303 | -487.6 | 222.36 | -52.2 | 75.3 | 60.20 | 55.6 | 2.58 |
| 313 | -489.8 | 230.03 | -57.8 | 81.8 | 63.93 | 57.5 | 2.67 |
| 323 | -521.4 | 295.54 | -78.4 | 96.0 | 63.40 | 73.9 | 3.43 |
| 2.0 | 293 | -428.7 | 420.50 | -187.5 | 169.4 | 91.89 | 105 | 4.88 |
| 303 | -350.6 | 557.82 | -156.5 | 159.9 | 61.56 | 139 | 6.47 |
| 313 | -373.4 | 574.30 | -164.0 | 139.6 | 57.01 | 144 | 6.67 |
| 323 | -397.3 | 581.92 | -131.9 | 125.1 | 47.90 | 145 | 6.75 |

The corrosion current or rates increased suddenly on passing the lowest CO_2 gas concentration stream in the concrete simulate solution, it became more than 8 times faster than electrolyte containing no CO_2 gas, and on increasing of solution temperature, the corrosion rates increased in a significant magnitude. On reaching CO_2 concentration of 2%, a corrosion rate of 4.88 mm/y was recorded at 20°C, which increased on heating to 50°C and became 6.75 mm/y. Figure (4) show the dependency of corrosion rates on the CO_2 gas concentration and temperature.
Figure 4. Corrosion rates of carbon steel reinforcing bar in artificial concrete solution with CO₂ gas at different concentration and temperature.

The behavior seems to have S-shape, which means the corrosion rate starts fast and then, a barrier layer is formed on the surface. Then this layer was grown and broken to retain again a fast rate of corrosion nearly at all temperatures.

Carbonation in the presence of moisture CO₂ is present in air reacts with Ca(OH)₂ to form CaCO₃, and causes the reduction in pH of pour water from between 12.6 to about 9.0 of CSRB in concrete forms a thin passivity layer of oxide. What remains only with high pH As the pH reduces the oxide layer is removed and the corrosion of steel starts, its volume increases and creates tensile stresses in concrete (13,14).

The following equations represent the reactions take place in presence of moisture and CO₂ (15,16).

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \] (Dil. Carbonic acid) \( \ldots(2) \)

\[ \text{H}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} \] \( \ldots(3) \)

The passive layer can be lost by carbonation due to reduction in alkalinity of the concrete. The products of corrosion occupy a volume as much as six times the original volume of steel (17).

The values of the calculated Rp increased with increasing CO₂ concentration which may be attributed to the carbonation of the surface and decreases the conductivity by formation of non-conductive oxide rust products on the CSRB surface.

The optical microscope images in Fig. (5) show the effect of CO₂ concentration on the microstructure of the polarized sample in simulate concrete solution. The order of increasing degree of defects of the surface of CSRB follows positively the concentration of the gas.

Figure 5. Optical microscopic images of CSRB polarized in CO₂ containing simulated concrete solution (0.03, 0.26, 0.5, 1.0, 1.5, and 2.0%).

The dark area in the above optical images increased with increasing corrosion rates due to increasing CO₂ concentration and highly supported the polarization measurements.

The AFM images in Fig. (6) give the same conclusion on the effect on CO₂ gas on the CSRB.
Figure 6. AFM 3D images of CSRB polarized in CO$_2$ containing simulated concrete solution (0.03, 0.26, 0.5, 1.0, 1.5, and 2.0%).

The pitting probability was examined by cyclic polarization of the CSRB in artificial concrete solution with flowing of CO$_2$ gas at different concentration at 20°C, no series sign of pitting recorded, as shown in cyclic polarization curves presented in Fig. (7);

Figure 7. Cyclic polarization curves of carbon steel reinforcing bar in simulate concrete solution containing different CO$_2$ gas concentration.

Conclusions:

The following conclusions are drawn from the findings of the current work:
1-The corrosion rate of the CSRB in artificial concrete greatly increases with the existence of CO$_2$ gas and highly depends on its concentration in the range 0.03 to 2.0%.
2-No sign for pitting corrosion is recorded at all CO$_2$ concentrations and the general corrosion is the main problem in the conditions under consideration.

Conflicts of Interest: None.

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دور ثاني أكسيد الكربون في تآكل قضبان تسليح الصلب الكربوني في محلول شبيه الخرسانة

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قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة:

العوامل الرئيسية التي تجعل حدوث تآكل حديد التسليح في الخرسانة ممكنا هي أيونات الكالسيوم وأتمتصات ثاني أكسيد الكربون من المحطات. ويعمل كل منهما حسب آلية معينة تؤدي إلى تضمين الطبقية الواضحة الموجودة على سطح حديد التسليح في الخرسانة. في هذا العمل، تم إجراء دراسة تأثير ثاني أكسيد الكربون في محلول الخرسانة الاصطناعي على سطح ديكاكينح لقياس تأثير حديد التسليح المصنوع من الصلب بطرقية فعالة باستخدام تيار من غاز ثاني أكسيد الكربون في تركيز مختلف تم تحايله بين 0.03 – 2.0%. وتم تأثير ارتفاع درجة حرارة محلول الأملاح، والتي تصل إلى 50 درجة مئوية. استخدمت محلولات تفاعل محلية لقياس تأثير الطاقة على التآكل. تم دراسة التغير في التركيب المحوري والاضطرابات السطحية لاستزاع من التآكل وسرعه التآكل والكربوني دون ثانيا في التآكل المجهري وتطور السطح. بعد الابتكار في محلول الخرسانة المحاكاة باستخدام المحال الطينية والقوة الذرية، تبين النتائج أن سرعة التآكل ازدادت بوجود غاز ثاني أكسيد الكربون، وهذا الانزلاق أدمت طريقة مع زيادة تركيز الغاز. لم يسجل وجود تآكل تقريبي لحديد التسليح في محلول الخرسانة الاصطناعي في جميع تركيزات غاز ثاني أكسيد الكربون. وان التآكل العام هو السائد في جميع الظروف تحت الدراسة.

الكلمات المفتاحية: الخرسانة الصناعية، غاز ثاني أكسيد الكربون، محلول الخرسانة، حديد التسليح.