UREA FERTILIZER AS CORROSION INHIBITOR FOR REINFORCED STEEL IN SIMULATED CHLORIDE CONTAMINATED CONCRETE PORE SOLUTION

Abdulrasoul Salih Mahdi1*

1Electrochemical Eng. Department, College of Engineering, Babylon University, Iraq

ABSTRACT

Urea is worldwide used in agriculture as a fertilizer. This paper presents an experimental study on the inhibition effect of urea fertilizer on corrosion of reinforced steel in concrete immersed in simulated concrete Pore (SCP) solution using open circuit potential and potentiodynamic polarization technique. SCP solution consist of 2% potassium hydroxide and 3% NaCl solution was used. Various percentage of urea from 0.2%, 0.5%, and 1% in SCP solutions were examined in this experiment. The open circuit potential tests showed that the potential of reinforced steel samples immersed in SCP solutions containing urea fertilizer was moved more positive than that in control sample.

Potentiodynamic polarization measurements showed a shifting in Corrosion potential (Ecor) toward positive direction and a decreased in corrosion current density (Icor), corrosion rate (CR) of steel samples immersed 2 hr and 7 days in SCP solutions containing urea inhibitor compared with control sample which is an indication of formation of protective passive film on steel surface and also indicate that urea fertilizer maintained stable passivity even in presence of aggressive chloride ions. Polarization curves showed that urea acts as mixed type inhibitor controlling the anodic reaction predominantly. The results explained that after 7 days of immersion in SCP solutions the highest inhibition efficiency was 86.15% at 0.5% urea concentration. Falling the inhibition efficiency of urea inhibitor to 72.6% at 1% concentration indicate that increasing the concentration is not useful and appropriate amount of inhibitor must be used. The experimental results of this paper showed that urea is an effective inhibitor, gave good corrosion inhibition for concrete reinforced steel immersed in SCP solutions during the period of this study.

Keywords: Urea Fertilizer, Reinforced Steel, Corrosion, Corrosion Inhibitor, Simulated Pore Solution.
INTRODUCTION

Corrosion of reinforced steel in concrete represents the major problem worldwide [1]. Reinforced steel corrosion happen mainly due to the penetration of chloride ions to steel surface which destroy the passive film that originally formed on the rebar surface due to the alkalinity of cement paste (PH 12.5–13.5) during concrete casting [2]. Chloride ions act as catalyst to corrosion when present in sufficient amount at rebar surface, they are not consumed in the process and permit the corrosion to proceed quickly in addition they are absorb and retain moisture which increase the water content in concrete pores solution and then increase the electrical conductivity of the concrete and accelerate the corrosion. [3]

\[
\text{Fe}^{2+} + 2\text{Cl}^- \rightarrow \text{FeCl}_2 \\
\text{FeCl}_2 + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 + 2\text{Cl}^-
\]

The deposition of corrosion products with a volume of two to four times the original steel in a restricted space around the rebar sets up an expansive stress which may crack and spall the concrete cover[4,5]. Corrosion prevention of concrete reinforced steel has been widely studied and various methods were suggested to delay, slow, or stop the corrosion of reinforcement and then enhance the service life of concrete structure such as cathodic protection, anodic protection, coating and inhibitors[6,7,8]. Corrosion inhibitors are a chemical substances that when added in small amount to concrete mix decrease or slow down corrosion rate by changing the surface condition of the reinforced steel, they are widely used as the most applicable and economical way to prevent corrosion of concrete reinforcement [9,10]. Most of corrosion inhibitors are classified as organic and in organic inhibitors according to its chemical nature and to anodic, cathodic or mixed inhibitors according to the electrochemical reaction on the steel surface and its environment [11].Corrosion inhibitors, both inorganic and organic, have been developed to prevent or slowing the corrosion rate of steel rebar . Many authors reported about using inorganic and organic inhibitors in corrosion prevention of concrete reinforced steel [12, 13, 14].

Inorganic inhibitors interfere with anodic or cathodic reaction of the corrosion process in order to form passive film on steel surface [15].Inorganic inhibitors were proved as one of the most effective in preventing corrosion of steel in concrete [16,17, 18], leaching problem toxicity, as well as their harmful environmental effect have highly reduced its applications [19, 20]. Organic inhibitors acting over the anodic or cathodic reaction or both to prevent the breakdown of the passive film by building a mono molecular film act as a barrier between the metal and the environments (water, oxygen, chloride ions) [21, 22, 23, 24]. Among the organic inhibitors the compounds that containing nitrogen, oxygen or sulphur atoms have been proven by several researchers to be effective in decreasing corrosion rate in acidic media, most of these compound form coordinated bond with the steel surface by electron transferring and then form complexes with iron which act as a protective film inhibit there bar corrosion[25,26]. Research efforts have been carried out to formulate environmental friendly acceptable, nontoxic organic corrosion inhibitors [27, 28, 29].

To evaluate the efficiency of inhibitors in preventing reinforced concrete steel from corrosion there are generally two methods, one uses actual concrete specimens and the other uses the simulated pore solution test [30].Several research papers have been investigated the corrosion behavior of reinforced concrete steel in simulated alkaline concert pore solutions (pH 12 -13.5), that mainly consist of saturated calcium hydroxide Ca (OH)2, sodium hydroxide NaOH and potassium hydroxide KOH [31-33], some researchers used a saturated calcium hydroxide alone to represent concrete pore solution[21,34-40],others used mixture from saturated calcium hydroxide and sodium hydroxide or potassium hydroxide and sodium hydroxide to simulate pore solution[19,30,41].In this research 2% KOH solution contain 3% NaCl (pH 13.46) was used to represent the alkalinity of chloride.
contaminated concrete pore solution (SCP solution).

Urea fertilizer is an organic compound containing two nitrogen atoms \([\text{CO} (\text{NH}_2)_2]\) and one oxygen atom, enabling it to decrease the corrosion rate of metals and alloys. Few research works were done on the corrosion inhibition of urea and its derivatives in seawater and acidic media \([27, 28, 42]\). Urea fertilizer is cheap and environmentally friendly, it is used widely and safely in agriculture as a fertilizer, so in this study urea was examined as a corrosion inhibitor for reinforced concrete steel immersed in simulated alkaline pore solution containing 3% NaCl salt using open circuit voltage measurements and potentiodynamic polarization technique.

**EXPERIMENTAL WORK**

**Reinforcement Steel Preparation**

The steel rebar was procured from a local supplier which is currently used as concrete reinforcement. For open circuit voltage, four test samples were made by cutting the reinforcing steel into pieces each with 5 cm length and 0.95 cm diameter. One end of the test specimen was soldered to copper wire in order to use as electrical connection. An abrasive grinder was used to remove the mill scales and rust stains. The specimens were washed thoroughly with deionized water, degreased with acetone and dried. 25 mm of the bar was defined as the exposed length and the remaining length painted with PVC resin. For potentiodynamic polarization tests, steel discs of 10 mm diameter were cuts from steel bar and then braded with abrasive grinder machine.

**Solutions preparation**

Urea fertilizer (locally produced) and potassium hydroxide KOH, Sodium chloride NaCl (analytical grade) was purchased from local supplier, in order to use in this work. KOH solution was prepared by stirring appropriate amount of solid KOH substance in de-ionized water to obtain 2% KOH solution to simulate the alkalinity of concrete pore solution. 3% NaCl was added to this solution to form SCP solution (control solution PH 13.46). 0.2%, 0.5% and 1% urea fertilizer were added to the SCP solution to form three urea inhibitor solutions. In this study four different solutions were prepared, the first one SCP solution (control solution) and the other three solutions were the urea inhibitor solutions.

**Electrochemical Measurements**

Open circuit potential and potentiodynamic polarization measurements were used in this study to evaluate the corrosion behavior of the reinforced steel in SCP solution with and without urea inhibitors.

**Open Circuit Voltage Measurement**

When corrosion starts, excess electrons liberate from the anode (reinforced steel) and tend to flow toward the cathode (external electrode) which give a negative voltage on voltmeter reading, so more negative voltage reading indicate higher corrosion process on the rebar surface. Open circuit voltage method only give indication about the corrosion activity at the time of measurement, it does not give any indication about the corrosion rate \([43, 44]\).

To show the corrosion inhibition of urea fertilizer, open circuit voltage tests were carried out for reinforced steel specimens in different SCP solutions. The first solution was a control solution, the other three solutions consist of the control solution with urea inhibitor at concentrations of 0.2%, 0.5% and 1% of solution respectively.

Open circuit voltage was measured at interval of 2 days for a period of 28 days using standard calomel electrode (SCE) as reference electrode and high impedance digital voltmeter to measure the voltage, the reference electrode was connected to the common terminal of the digital voltmeter, whereas the reinforced steel (working electrode) was connected to the +ve terminal to get a
complete electrical circuit. The more negative reading of the voltmeter means the high corrosion activity on the reinforced steel at the time of experiments, according to this method if the potential is more than -0.276 V (SCE) the probability of active corrosion is very high (95%). Potential less than -0.126 V (SCE), very high probability of no corrosion. Potential in the range of - 0.126 V to -0.276 V, approximately 50% probability of corrosion, and potential more than -0.426V indicate severe corrosion condition [45].

**Polarization measurements**

Polarization measurements were carried out with Wenking M Lab Potentiostat Galvanostat instrument (GERMAN origin) under potentiodynamic conditions. This instrument itself is having programs to evaluate corrosion parameters such as corrosion current (Icorr), corrosion potential (Ecorr), anodic Tafel slope (ba) and cathodic Tafel slope (bc). Three electrode cell consist of a specimens as a working electrode, Ag/AgCl electrode as a reference electrode, and Platinum wire as a counter electrode was used in this experiment. The working electrode was rebar steel disk axially embedded in a Teflon holder to offer a flat disc shaped exposed surface area of 0.785 cm$^2$. The steel discs were mechanically polished with different grades of emery papers up to mirror finish, degreased with acetone then rinsed with distilled water and dried before each electrochemical experiment. Control specimen was immersed in SCP solution and the other specimens immersed in SCP solution containing urea fertilizer inhibitor at concentrations of 0.2%, 0.5% and 1% respectively. The experiments were performed after 2 hour of immersion as initial, and 7 days of immersion as final to verify the stability of passive film in presence of corrosive chloride ions.

Potentiodynamic polarization curves were conducted by changing the electrode potential automatically ± 250 mV around the open circuit potential at a scan rate of 1 mV/s. From Tafel plot corrosion parameters such as Ecorr, Icorr, ba and bc were recorded. Corrosion rate (mmpy), corrosion inhibition efficiency (IE %) was calculated and reported using the following equations[21].

$$\text{IE} \% = \left(\frac{I_0 - I}{I_0}\right) \times 100$$

Where:
- Equivalent weight of steel=27.93 gm,
- Steel density = 7.8 gm/ cm$^3$,
- Icor= current density mA/ cm$^2$
- IE = inhibition efficiency
- I$_0$ and I are the corrosion current density without and with the inhibitor respectively.

**RESULTS AND DISCUSSION**

**Open Circuit Potential Measurements**

Figure 1 shows the variation of open circuit potential of concrete reinforced steel with exposure time for the SCP solution (control solution) and SCP solutions containing 0.2%, 0.5%, and 1% urea respectively. For the first sixteen days of the exposure period, it was observed that the reinforced steel sample in control solution showed active corrosion condition with a potential reading increased from-0.38 v to -0.53 v (SCE), this is an indication of anodic reaction and then corrosion occurred at the steel surface due to the attack of chloride ions that presents in alkaline medium around the steel rebar. From about the day 17 to the day 23 the potential shifted toward the less active region (from -0.53v to -0.4v), this is may be the corrosion product that accumulated on the steel surface stifled the corrosion reaction [44]. Again the potential shifted toward the active region after the day 23, potential of -0.49v at the day 26 indicate that the corrosion started increasing may
be due to the dissolution of corrosion products leaving iron surface exposed again to the chloride ions which succeeded in destroying the passive film.

On the other hand the figure showed that the potential readings of steel rebar immersed in solutions containing 0.2% , 0.5%, and 1% urea fertilizer moved gradually toward the passive region with fluctuation indicating a passive film building up due to the inhibition effect of urea fertilizer with these concentration compared with the control sample during the time of the experiment and it is clear from the figure that the corrosion inhibition of urea fertilizer was more effective starting from the day 16th till the end of the experiment. This is may be due to the thickening of the protective film at that time.

![Figure 1: potential variation of reinforced steel samples with the exposure time in chloride contaminated simulated pore solutions with and without urea inhibitor](image_url)

**Potentiodynamic polarization**

Tafel polarization curves of reinforced steel samples in SCP solution without and with various concentration of urea inhibitor for 2 hr immersion are shown in figures 2. Corrosion current (Icor), corrosion potential (Ecor), anodic Tafel slope (ba) and cathodic Tafel slope (bc) were measured from Tafel plots, Corrosion parameters such as corrosion rate (CR), inhibition efficiency (IE %) were calculated from the measured parameters. All of these parameters were reported in table 1. The table shows that the Icor and CR values of reinforced steel sample in control solution is 20.19 µA/cm² and 0.236 mmpy respectively, they decreased in the presence of urea inhibitor, the lower value of 5.26 µA/cm² for Icor and 0.062 mmpy for CR was achieved at concentration of 0.5% urea. Corrosion inhibition efficiency is 64.53% for 0.2% urea, 85.53% for 0.5% urea solution and 70.28% for 1% urea solution, this observations indicate that maximum inhibition efficiency was achieved at 0.5% urea concentration and the increasing urea concentration to 1% decreased the inhibition efficiency to 70.28%, this may be at higher concentration of inhibitor the passive film formed (Fe+2 – urea complex) on steel surface goes to the solution which lead to weak protective film [44]. Furthermore it is clear from the table that the reinforced steel corrosion potential immersed in SCP solution (control solution) was (- 462.4 mV Ag-AgCL) and the presence of urea fertilizer with various concentration in SCP solution shifted the potential toward the more positive direction (-414.8 mV Ag-AgCL for 0.2% urea, -379 mV Ag-AgCL for 0.5% urea, and -414.9 mV Ag-AgCL for 1% urea), in addition there was a decreasing in the corrosion current density due to the presence of inhibitor. This is an indication that urea fertilizer control the anodic reaction predominantly [19, 45]. Also the decreasing of anodic Tafel slopes values (ba) with increasing inhibitor concentration indicate that urea fertilizer act as mixed type inhibitor inhibited iron dissolution at anodic site by
forming a protective passive film (Fe²⁺ – urea complex) on the steel surface and control hydrogen evolution process at the cathodic site [46, 47].

Figure 2: Tafel polarization curves of the reinforced steel after 2 hr immersion in the SCP solutions without and with various concentrations of urea fertilizer inhibitor

Table 1: Polarization parameters for reinforced concrete steel after 2 hr immersion in the SCP solution without and with different concentrations of urea inhibitor

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{\text{cor}}$ mV</th>
<th>$I_{\text{cor}}$ µA/cm²</th>
<th>$b_a$ mV/dec</th>
<th>$b_c$ mV/dec</th>
<th>CR mmpy</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-462.4</td>
<td>20.19</td>
<td>456</td>
<td>251</td>
<td>0.236</td>
<td></td>
</tr>
<tr>
<td>Control +0.2% urea</td>
<td>-414.8</td>
<td>7.16</td>
<td>288.6</td>
<td>218.7</td>
<td>0.083</td>
<td>64.53</td>
</tr>
<tr>
<td>Control +0.5% urea</td>
<td>-378.3</td>
<td>5.26</td>
<td>286.4</td>
<td>250.9</td>
<td>0.062</td>
<td>83.53</td>
</tr>
<tr>
<td>Control +1% urea</td>
<td>-414.6</td>
<td>6</td>
<td>241.4</td>
<td>294</td>
<td>0.07</td>
<td>70.28</td>
</tr>
</tbody>
</table>

Corrosion parameters such as $E_{\text{cor}}$, $I_{\text{cor}}$, $b_a$, $b_c$, corrosion rate (mmpy), IF % for the steel samples exposed to various inhibitor system for 7 days were measured and calculated from Tafel plots and reported in table 2 and shown in figure 3. The table shows that $I_{\text{cor}}$ and CR values for samples immersed in SCP solution containing urea fertilizer decreased higher than that after 2hr immersion, the lower values of $I_{\text{cor}}$ (2.77 µA) and CR (0.0324 mmpy) was achieved at 0.5% urea. $E_{\text{cor}}$ of steel samples in urea inhibitor system also moved toward noble side and $b_a$ decreased with increasing inhibitor concentration. This is an indication that the urea inhibitor maintained stable passivity even in the presence of aggressive chloride ions. This results indicate that urea has ability to be a good corrosion inhibitor for reinforced concrete steel, the inhibitive power of urea may be due to the presence of the nitrogen and the oxygen atoms in its structure which give it the ability to enhance the inner protective layer of $\gamma$Fe3O4 that originally formed on the steel surface due to the high alkalinity of pore solution by forming protective outer layer of urea – Fe²⁺ complex [21, 42]. Maximum efficiency of 86.25 % was achieved at urea concentration of 0.5% urea. Decreasing inhibition efficiency to 72.6 % with increasing urea concentration to 1 % indicating that increasing the concentration is not useful and appropriate amount of inhibitor must be used [25].
Figure 3: Tafel polarization plots of reinforced steel after 7 days of immersion in SCP solution with and without urea fertilizer inhibitor

Table 2: Polarization parameters for reinforced concrete steel after 7 days immersion in SCP solution with and various concentrations of urea inhibitor

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{\text{cor}}$ (mV)</th>
<th>$I_{\text{cor}}$ (µA/cm²)</th>
<th>$b_a$ (mV/dec)</th>
<th>$b_c$ (mV/dec)</th>
<th>CR (mmpy)</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-464.9</td>
<td>20</td>
<td>456.4</td>
<td>242.7</td>
<td>0.234</td>
<td></td>
</tr>
<tr>
<td>Control + 0.2%</td>
<td>-416.3</td>
<td>7.24</td>
<td>291.1</td>
<td>218.6</td>
<td>0.085</td>
<td>63.8</td>
</tr>
<tr>
<td>Control + 0.5%</td>
<td>-296.6</td>
<td>2.77</td>
<td>278.6</td>
<td>231.1</td>
<td>0.0324</td>
<td>86.15</td>
</tr>
<tr>
<td>Control + 1%</td>
<td>-345.8</td>
<td>5.48</td>
<td>234.7</td>
<td>199.4</td>
<td>0.064</td>
<td>72.6</td>
</tr>
</tbody>
</table>

CONCLUSION

From this study the following can be concluded:

1- Urea fertilizer can be used as eco-friendly inhibitor decrease efficiently the corrosion rate of concrete steel.
2- Urea fertilizer that was used in this study at 0.2%, 0.5%, 1% concentrations respectively was effective for corrosion inhibition of mild steel reinforcement immersed in simulated concrete pore solution containing 3% sodium chloride at the ambient temperature.
3- The best result and hence the best corrosion inhibition performance of the steel reinforcement was obtained in this work with 0.5% urea concentration, the inhibition efficiency after one week of immersion in test solution was 86.15% and corrosion rate was 0.0324 mmpy.
4- Appropriate amount from the urea inhibitor must be used since increasing the concentration to 1% gave low inhibition efficiency and high corrosion current and corrosion rate.
5- Tafel plots of reinforcement steel in SCP solution with and with urea showed that urea act as a mixed inhibitor control anodic reaction predominantly by forming F+2 – urea complex on anodic side.
6- Studies with actual concrete specimens are needed to know the effect of urea fertilizer on the compression strength of the concrete.
7- Long time studies are needed to make final recommendations about the dose of these inhibitor for the protection of concrete reinforced steel.
REFERENCES


