Studying the Effect of Eco-addition Inhibitors on Corrosion Resistance of Reinforced Concrete

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Abstract: Due to the high cost of repair of damaged constructions, some preventive measures, namely using, for example, rice husks as corrosion inhibitor admixtures were chosen as a prospective preventive technique. Along this approach, laboratory concrete samples were so prepared and sent to mechanical testing, and concurrently, the inhibitive potential of the rice husks suspended in electrolyte solution (water with dissolved sodium chloride of 3.5 wt.%) was also tested by using a standard electrochemical corrosion testing technique, i.e. the powdered rice husk was added to the electrolyte solution in different dosages (1%, 2% and 3%), then the corrosion currents of the steel samples were recorded by using a three-electrode cell assemblage. In these laboratory tests a quite steady decreasing tendency could be observed in the measured corrosion current densities ($I_{corr}$) compared to the case when the electrolyte solution did not contain any inhibitor admixture ($I_{corr}=41.3 \mu A/cm^2$; taken as the reference). For example, a corrosion current of $I_{corr}= 28.5 \mu A/cm^2$ was measured at 1% rice husk concentration, and only $I_{corr}= 7.8 \mu A/cm^2$ when the solution was mixed with 3% rice husk powder.

Keywords: Eco Inhibitor, Corrosion, Concrete

1. Introduction

Corrosion of reinforcing steel and other embedded metals is the leading cause of deterioration in concrete. When steel corrodes, the resulting rust occupies a greater volume than the steel. This expansion creates tensile stresses in the concrete, which can eventually cause cracking, delamination, and spalling, see Figure 1 [1]. Steel corrodes because it is not a naturally occurring material. Rather, iron ore is smelted and refined to produce steel. The production steps that transform iron ore into steel add energy to the metal. Steel, like most metals except gold and platinum, is thermodynamically unstable under normal atmospheric conditions and will release energy and revert back to its natural state—iron oxide, or rust. This process is called corrosion [2].

For corrosion to occur, four elements must be present: There must be at least two metals (or two locations on a single metal) at different energy levels, an electrolyte, and a metallic connection. In reinforced concrete, the rebar may have many separate areas at different energy levels. Concrete acts as the electrolyte, and the metallic connection is provided by wire ties, chair supports, or the rebar itself. This initial precipitated hydroxide tends to react further with oxygen to form higher oxides. The increases in volume as the reaction products react further with dissolved oxygen leads to internal stress within the concrete that may be sufficient to cause cracking and spalling of the concrete cover [3]. The rate of corrosion can be reduced by using corrosion inhibitors. These inhibitors are chemical compounds that reduce the corrosion rate of metals existing in actively corrosive environments [4]. Recent researches shown that green inhibitors are more environmental benign than organic and inorganic inhibitors. The alternative way to minimize the risk of organic and inorganic inhibitors is the adoption of green inhibitor to reduce the environmental hazard [5-6]. Extracts of plant materials contain a wide variety of organic compounds. The natural constituents of these extracts contain N, O, and S containing heterocyclic macromolecules, which when reaching the steel surface by diffusion and get adsorbed at the steel concrete interface by secondary molecular interaction with the metal and metal oxide and at the steel
rebar they can form protective layers to repeal water molecules and inhibit ingestion of destructive species like Cl\(^-\), SO\(_4^{2-}\), and CO\(_2\) which are responsible for the depassivation of steel [7-8].

Figure 1. Corrosion of reinforcing steel is the most common cause of concrete deterioration [1].

It is believed that common steel rebars in contact with aqueous electrolyte solutions containing dissolved oxygen as well will corrode in a relatively wide pH (both acidic and slightly alkaline) ranges, but iron (and steel) are more or less “inert” or “passive” as long as the concrete pore solution’s pH is highly basic and it does not contain much “aggressive” anions like chlorides. However, the pore solution pH might change (e.g. through carbonation) and can dissolve oxygen from air and salts (e.g. NaCl) from the environment (e.g. in seashore regions). Therefore, incorporation into the structure of concrete some adequate inhibiting components appears to be a clever approach to mitigate the rate of corrosion. Such chemical compounds (also the ones used for steels) often have good adsorptive properties and it is also true for several extracts of organic matter (extracts of herbs, leaves, seeds) as they contain polysaccharides and compounds with heterocyclic rings having functional groups like –OH, –COOH, –NH\(_2\), –SH, –SO\(_3\)H. And, such water soluble compounds and their radicals can strongly interact with the surface of metals and block the cathodic and/or anodic corrosion sites and/or form thin protective films, and all of such surface effects may eventually reduce (i.e. inhibit) the rate of corrosion. Interestingly, although this novel idea came to life only for a few years ago, but there are even some review papers [2, 3] and books published in this topic by now. However, there are still many open questions and much room for further detailed scientific studies in this field. One rational approach towards the selection, for example, of the “best” green inhibitors seems to trying to identify those organic components of the plant extracts which can function in a similar fashion to the synthetic (and sometimes toxic) inorganic chemicals proved being effective and are available on the market. Such commercial ‘organic type’ so-called migrating inhibitors (MCIs) mostly contain amines, alkolamines and carboxylic part as it is illustrated in Table 1. [9-11].

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Name of product</th>
<th>Chemical ingredients disclosed in the MSDS(^*)</th>
<th>Type of ingredient</th>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cortec</td>
<td>MCI 2021 &amp; 2022 [88]</td>
<td>Aminocarboxylates (\text{**)}</td>
<td>Not given</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MCI-2006NS [89]</td>
<td>Sodium salt of oxycarboxylic acid</td>
<td>Aminocarboxylates</td>
<td>30 – 60</td>
</tr>
<tr>
<td>BASF</td>
<td>MCI-2020 [90]</td>
<td>3-aminoalkyltriethoxysilane</td>
<td>3-aminoalkyltriethoxysilane</td>
<td>&lt; 10</td>
</tr>
<tr>
<td></td>
<td>FerroGard 903, Norway [91]</td>
<td>2-aminoethanol</td>
<td>Alkanolamine</td>
<td>5 – 10</td>
</tr>
<tr>
<td>Sika</td>
<td>FerroGard 903, Canada [92]</td>
<td>Ethyl alcohol</td>
<td>Ethyl alcohol</td>
<td>1 – 5</td>
</tr>
</tbody>
</table>

Table 1. Representative examples of commercial migrating corrosion inhibitors (MCIs) for concrete [12].
The application of inhibitors to the reinforced concrete structure can be done during mixing of concrete or can be applied on the surface of already existing reinforced structure for repair works. Inhibitors can be both organic and inorganic depending on their use. Organic inhibitors include extracts from plants. The advantage of green inhibitor over chemical inhibitors as they are readily available, less toxic, biodegradable, do not contain heavy metals, environmentally friendly and easily renewable. The inhibitors not only participate in reducing the rate of corrosion but it also takes part in the properties like compressive strength of the structure. Inhibitors are a chemical substance or extracts from plant, when added in small concentration delays the rate of corrosion. They form a hydrophobic film on the surface of reinforcement by adsorbing either ions or molecules of inhibitors on the surface. It reduces the corrosion of reinforcement by blocking cathodic or anodic reaction. The use of inhibitors is simple and economical with good inhibiting effect. The effectiveness of inhibitors depends mainly on the concentration of inhibitor, more the concentration more is the inhibitor effect on corrosion. The application requires transport of inhibitor to the reinforcement where it has to reach sufficiently on the surface to protect the steel against corrosion or to reduce the rate of ongoing corrosion. The application of inhibitor does not require any skill it only depends on adding of inhibitor in proper proportion [13-14].

2. Methodology

2.1. Materials

2.1.1. Cement
Ordinary Portland cement type I locally available was used conforming to the Iraqi specification IQS No. 5/1984.

2.1.2. Fine Aggregate
Graded sand was used. The sieve analysis, Mud %, SO₃ % and Fineness modulus according to IQS 45:1984 specification.

2.1.3. Coarse Aggregate
Graded gravel used in this study. The sieve analysis, Mud %, SO₃ % and limits according to specification for IQS 45:1984.

2.1.4. Water
Tap water was used throughout this work for both making and curing the specimens.

2.1.5. Natural Corrosion Inhibitors (Rice Husks)
The production of rice leaves rice husks as a waste material, which may be utilized as inhibitors of corrosion. It takes five tons of rice paddy to produce one ton of rice husk waste, and it takes approximately 100,000 tons of rice husk per year.

2.1.6. Steel Reinforcement
The steel reinforcement that was used in this work was wires of 0.5 cm in diameter. These wires were cleaned with wetted grinding paper (rough then smooth) then immersed in cleaner liquid (flash liquid) to remove any rust or deposits on their surface.

2.2. Concrete Mixes
Concrete mixes were designed in accordance with the American mix design method (ACI 211) to have a compressive strength 30 MPa at age of 28 days. Ordinary Portland cement concrete mix with cement: sand: gravel ratio of 1: 1.64: 2.57 and water / cement ratio of 0.42 was prepared for casting specimens. The materials were mixed by using an electrically driven batch mixer.

Ten types of concrete mixes were prepared throughout this study:
1. Reference concrete mix without any admixture.
2. Three concrete mixes containing rice husks in three concentrations (1, 2 and 3% by weight of cement).

2.3. Preparation, Casting and Curing of the Test Specimens
Specimens were prepared as cubes with 150*150*150mm reinforced concrete specimens for electrochemical tests. The reinforced concrete samples cured in tap water for a period 30 days with immersed partially in 3.5% NaCl solution for electrochemical tests.

2.4. Electrochemical Tests (Linear Polarization Resistance of Steel Reinforcement in Concrete)
The tester consists of electrochemical corrosion test cell and electrodes. The cell made from materials anticorrosion as glass and the shape of the cell was seems- spherical with volume 1000 ml. The cell contains three electrodes are: Working electrode, Auxiliary electrode and reference electrode as shown in Figure 2. Drawing the polarization curve anodic and cathodic has been automatically control by computer which communicated with Potentionstat and by used the program (Bank-Elechtionies) to drawing the curves. The Tafel tester type (MLab 100, power 35 W) to test electrochemical corrosion

Figure 2. Concrete sample connecting with Tafel tester.
3. Results and Discussion

1-Sample without Inhibitor (Reference)
The samples of test cured in tap water for a period 30 days with immersed partially in 3.5% NaCl solution. Figure 3 shows that sample have: \( I_{corr} = 41.25 \mu A/cm^2 \).

2- Sample with Rice Husks Inhibitor
The samples of test in three concentrations (1, 2 and 3% by weight of cement) cured in tap water for a period 28 days with immersed partially in 3.5% NaCl solution. Figure 4 shows that sample (1% by weight of cement) have: \( I_{corr} = 28.54 \mu A/cm^2 \).

Figure 5 shows that sample (2% by weight of cement) have: \( I_{corr} = 9.94 \mu A/cm^2 \) and Figure 6 shows that sample (3% by weight of cement) have: \( I_{corr} = 7.76 \mu A/cm^2 \).
The calculated corrosion current densities indicate a relatively strong inhibitive effect of the rice husks powders mixed with the fresh concrete that shows the ability of the tested inhibitor to form a protective layer around steel surface.

4. Conclusions

1. Better corrosion resistance in the samples is at a ratio 3% of the rice husks.

2. The economic cost of rice husks are almost nothing compared to industrial inhibitors so it is considered the best.

References

[1] ACI Committee 222, Protection of Metals in Concrete Against Corrosion, ACI 222R-01, American Concrete Institute, Farmington Hills, Michigan, 2001.


