



# Corrosion behavior of galvanized steel due to typical soil organics



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## HIGHLIGHTS

- Organic content should not be treated as a single entity in soil corrosion studies.
- Corrosion behavior of galvanized steel depends on the composition of soil organics.
- Citric acid is able to completely dissolve the protective zinc layer.
- Increasing content of humic and oxalic acids form layers that block corrosion.

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## ABSTRACT

The corrosion behavior of galvanized steel due to organics typically found in soils is addressed in this exploratory study by means of the open circuit potential and the potentiodynamic polarization tests in solutions of humic compounds, carbohydrates, and carboxylic acids. Subsequently, the surface is characterized with Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy. The data shows that the corrosion effect of organic matter depends on its composition and concentration. Citric acid is the most corrosive organic. Humic acid and oxalic acid produce higher current densities at the lowest concentrations and promote the formation of physical barriers at higher concentrations that reduce exposure to the corrosive environment.

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## 1. Introduction

This study aims to determine if soil organics play a significant role in promoting corrosion of galvanized steel reinforcements in Mechanically Stabilized Earth (MSE). MSE is a civil infrastructure technology for retaining walls whose use has increased significantly since its introduction to the construction practices in North America in the 1970s due to its technical and economic practicality in front of the cast-in place type of walls. MSE walls have three major structural components: (1) a level pad; (2) a succession of layers of backfill soil and reinforcements; (3) and a vertical face element. The second component in the list is where the galvanized-steel reinforcements are in direct contact with soil.

Galvanized steel is widely employed in numerous engineering applications due to its resistance to corrosion. This improved corrosion behavior is given by the zinc coating in two steps: first, acting as physical barrier, and secondly, providing galvanic protection

[1]. The physical barrier isolates the steel from the environment through two distinct layers during the different stages of the corrosion process. The first barrier is the zinc coating itself, which is progressively replaced in its isolation function by the formation of a layer of zinc corrosion products. The galvanic protection means that even if the steel substrate gets exposed, the zinc layer will corrode preferentially [2]. The corrosion of galvanized steel has been described as a three-stage process [3,4]. In the first stage, solid zinc corrodes, releasing divalent ions ( $Zn^{2+}$ ). The zinc corrosion products, composed mainly of zinc oxide, form an adherent and porous layer that has a characteristic white color [5]. The galvanic protection that zinc provides to steel occurs in this stage when small areas of the steel are exposed to the environment due to scratches or other imperfections of the coating [6,7]. In the second stage, the layer of corrosion products grows until zinc is depleted and a thick, porous, and non-protective layer of corrosion products is formed. The main component of this layer is zinc hydroxide:  $Zn(OH)_2$ . During this stage, the corrosion front reaches the Zn–Fe alloy layer and the galvanized steel experiences a shift of its corrosion potential to more noble values. In the third stage, corrosion of steel initiates and iron ions are released ( $Fe^{2+}$ ). The iron corrosion products,

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which could be any of the ones that have been identified for galvanized steel (FeO, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe(OH)<sub>2</sub>, and Fe(OH)<sub>3</sub>) become visible as red rust [8].

Civil applications, such as MSE walls, culverts, or pipes require galvanized steel to be buried or in contact with soil. This is a highly inhomogeneous environment because it exhibits a wide range of physical and chemical properties that synergistically influence the long term performance of galvanized steel buried in it [5]. Some of the factors that have been acknowledged as determinant in the corrosion aggressiveness of soils are pH, resistivity, moisture content, temperature [9,10], oxygen availability [11,12], and soluble salt concentration [13,14]. Yet, an important factor behind the differences in soil properties lies in the variety of chemical compounds that they contain. For instance, the organic content, whose presence distinguishes soil from decomposed rock, may vary from 0.10% in desert soils to almost 100% in organic soils [15,16]. In studies of underground corrosion, however, the organic content is often treated as a single general entity that intervenes in the corrosion of metals only by providing nutrients to bacteria that participate in the Microbially-Influenced Corrosion process [17–19]. Although this is certainly a relevant role of organics, such approach overlooks the complexity of the composition of organics in soil and the implications that the properties of each kind of organic could have on corrosion.

The composition of soil organic matter has itself been the object of numerous studies that agree that the non-living fraction, which accounts for about 95% of it, is more important for the soil chemistry than the living fraction [19,20]. The bulk of this non-living fraction is humus, completely decomposed material that can be further classified into humic compounds and non-humified material. The humic compounds are humic acid, fulvic acid and humin, which together represent up to 70% of humus and are responsible for the yellow to brown color of soil [21]. The complement of the non-living fraction is non-humified material, whose major components are carbohydrates and lipids that represent, respectively, from 10% to 30% and from 2% to 6% of humus [22]. The remainder fraction of non-humified material is a combination of various types of organics that are present in minute amounts. In particular, organic acids, which may be found in concentrations that range from 10<sup>-2</sup> to 5 mM are relevant because they are the most corrosive organic species.

In this study, four organic reagents were selected to account for the main soil organic components: Humic acid to represent humic substances, dextrose to represent carbohydrates, and oxalic acid and citric acid to account for organic acids.

Data of the corrosion of metals due to organic compounds is scarce in general, and to the best of our knowledge, non-existent for galvanized steel. This paper aims to determine the relevance of organics typically found in soils as corrosion promoters of galvanized steel. Moreover, it is expected to fill the gap in literature of electrochemical results of galvanized steel due to organics.

## 2. Experimental procedures

### 2.1. Materials

The material used was a low carbon, cold-rolled galvanized steel sheet with a thickness of 0.03 cm and a coating thickness of 20 μm ± 2 μm. Solutions of humic acid, dextrose, oxalic acid and citric acid were prepared for the electrochemical tests at concentrations of 0.01, 0.10, 0.25, 0.50, and 1.00 wt%.

### 2.2. Test methods

#### 2.2.1. Solution characterization and electrochemical measurements

The test solutions were initially characterized by measurements of their pH and conductivity. Then, measurements of the open circuit potential (OCP) were conducted to ensure that the samples reached a stable state before initiation of the electrochemical analysis. The potentiodynamic polarization (PDP) test was

employed to determine if variable concentrations of the selected organics would modify the kinetic parameters, corrosion potential and current density of galvanized steel. Each electrochemical test was performed three times for each one of the five concentrations and for each organic reagent in order to confirm repeatability of the results. For each run, a fresh solution and a fresh galvanized steel sample were used. All samples were cleaned with ethyl alcohol and dried prior to immersion in the test solution. The electrochemical corrosion tests were carried out in a conventional three-electrode corrosion cell where the galvanized steel samples were placed in a sample holder so that only a surface of 1 cm<sup>2</sup> remained exposed to the environment. The counter electrode was a graphite rod and the reference electrode was silver/silver chloride (Ag/AgCl). The cell was placed on a magnetic stirrer with a rotating speed of 300 rpm to produce a vortex at the electrode. The temperature of the cell was maintained constant at 25 °C using a VWR water bath. The measurements were taken with a Princeton Applied Research VersaStat 4 potentiostat. The PDP tests were performed from -0.25 V Ag/AgCl to +1.00 V Ag/AgCl with respect to the OCP, with a scan rate of 0.166 mV/s.

#### 2.2.2. Surface characterization

After conducting the electrochemical tests, the samples were extracted from the solution, rinsed with deionized water, and dried. The morphology of the surface and the corrosion products were observed with the Scanning Electron Microscope (SEM), followed by the Energy Dispersive X-ray Spectroscopy (EDX) technique that was used to determine the elemental composition of different areas of the surface. This method helped to confirm the extent of corrosion.

## 3. Results and discussion

The pH and conductivity of the solutions were fixed by the experimental conditions and measured prior to commencement of the electrochemical tests (Tables 1 and 2). Each organic solution exhibited a characteristic pH that was rather independent of concentration; whereas their conductivity increased as a function of concentration. Humic acid solutions were alkaline with pH near 10; dextrose solutions were neutral with pH around 6.8; and solutions of citric and oxalic acids were acidic, with pH values close to 3 and 2.3, respectively. Between 0.01 wt% and 1.00 wt%, the conductivity increased 63.5 μS for humic acid solutions, 36 μS for citric acid, and 523.5 μS for oxalic acid. In dextrose solutions the conductivity remained virtually constant at all concentrations and was almost negligible with a value of 0.3 ± 0.2 μS. In Fig. 1, it is observed that at most concentrations, the conductivity of humic acid solutions was higher than that of citric acid solutions, and that oxalic acid solutions exhibited the highest conductivity at all concentrations.

### 3.1. OCP results

The open circuit potential (OCP) was measured from the moment immediately after immersion until a stable potential was observed, which, for most solutions occurred within one hour. Fig. 2 shows the OCP curves for galvanized steel immersed in the four organic solutions.

In humic acid solutions (Fig. 2a) the potential shifted at all concentrations towards more noble values before stability was reached. The increase of potential was approximately 50 mV for most concentrations (0.01–0.50 wt%). Only for the highest concentration of 1.00 wt% the increase was smaller, about 20 mV. Also, as the concentration increased, the stable potential values became more negative, from -730 mV at 0.01 wt% to -840 mV at 1.00 wt%.

In dextrose solutions (Fig. 2b), the trend of the OCP curves at all concentrations showed a slight shift towards more negative values before the potential shifted towards more noble values. Nevertheless, it should be noted that the change in potential values from the beginning of the measurement until stability was reached was narrow, approximately 40 mV. In comparing the curves based on the solution concentration, it is observed that the solution with the highest concentration of 1.00 wt% exhibited the most noble stable potential value of -820 mV.

OCP curves of citric acid solutions (Fig. 2c) were characterized at all concentrations by a uniform decrease of potential of about

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